ANNUAL PROGRAM REVIEW

CHEMICAL RECOVERY AND CORROSION

March 24-25, 1999

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March 24-25, 1999

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DUES-FUNDED PROJECT SUMMARY

Project Title:	Control of Evaporator Fouling
Project Code:	
Project Number:	F016-02
PAC:	Chemical Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	W. Schmidl, N. DeMartini, J. Frederick,
Staff:	M. Amundsen, A. Martin
FY 99 Budget:	$79,000
Allocated as Matching Funds:	$59,000
Time Allocation	
Faculty/Senior Staff:	W. Schmidl (20%); N. DeMartini (40%), J. Frederick (5%)
Support:	M. Amundsen, (30%), A. Martin (10%)
Supporting Research	
M.S. Students:	G. Lansdell (MS candidate)
Ph.D. Students:	None
External:	R. Rousseau, J. Hseih, J. Smith (PhD candidate), GIT
RESEARCH LINE/ROADMAP:	Improved Capital Effectiveness. 8. Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.

PROJECT OBJECTIVES:

The first objective is to obtain data on the current state of black liquor evaporator fouling through a survey of the industry's evaporators. The second objective is to understand the causes of scale formation in black liquor evaporators and high solids concentrators. The third is to provide design data and guidance tools to reduce fouling (and thereby increase evaporator capacity) through improved design and operation.

PROJECT BACKGROUND:

This project was begun in FY98, in response to industry demand for improved capacity in black liquor evaporators and high solids concentrators. At an IPST organized meeting of industry representatives in May, 1997, it was decided that the most critical issue was soluble scales in high solids black liquor concentrators, and that this problem needed to be solved first. $CaCO_3$ scaling of black liquor evaporators, especially in mills where modified kraft pulping technologies are used, was also recognized as a critical problem.

A three-pronged approach has been taken in the initial six months of this work. First, a survey of black liquor evaporator fouling problems in North American kraft pulp mills was undertaken. Second, advanced chemical equilibrium modeling methods were employed to predict the solubility behavior of sodium salts in black liquor as it is concentrated to high dry solids contents. Third, an experimental program was begun to obtain experimental data on the solubility of sodium salts in black liquor at high dry solids contents.

SUMMARY OF RESULTS FOR FY99:

1. Evaluation of Scale Control Options in Falling-Film Black Liquor Evaporators and High Solids Concentrators

As black liquor is concentrated to total solids contents approaching 50% and above, two transitions occur. The first is the onset of precipitation of Na_2CO_3 and Na_2SO_4 as finely divided particles, ~0.5 μm, of a double salt, burkeite ($\sim 2Na_2SO_4 \cdot Na_2CO_3$) – this is the ***first critical solids*** point. Most black liquors contain more Na_2CO_3 than Na_2SO_4 – typically 2/1 to 4/1 on a mass basis. As black liquor is concentrated further, above the first critical solids point, roughly two moles of Na_2SO_4 are precipitated for every mole of

Na_2CO_3. The dissolved Na_2SO_4 is depleted, leaving the liquor rich in dissolved Na_2CO_3. Eventually, a ***second critical solids*** point is reached where Na_2CO_3 co-precipitates with Burkeite. This point can vary widely based on the composition of the liquor. Also, the precipitation rate at the second critical solids point is significantly higher than before it, and much larger particles, ~0.5 mm, are produced.

Our work to this point has shown that, for falling film evaporators, soluble scale deposition is worst in the effect where the transition from burkeite precipitation to Na_2CO_3 precipitation occurs, and in higher solids effects. We believe that, when the second critical solids point is exceeded in a falling film evaporator or concentrator effect, soluble scale fouling is very likely to occur.

The chemical equilibrium software that we have been using to investigate the solubility behavior of sodium salts in black liquor have proven to be very useful tools for diagnosing soluble scale problems in falling film evaporators and high solids concentrators. Table 1 compares the predicted second critical solids points for falling film evaporators from two different kraft mills with the locations where soluble scale fouling was observed. The critical solids points in Table 1 were predicted using the NAELS chemical equilibriium software, and were calculated at the product liquor temperatures from the respective effects.

Table 1. Comparison of the predicted second critical solids points for falling film evaporators from two different kraft mills with the locations where soluble scale fouling was observed.

Mill	A	B
Effect fouled[1]	1st	1st
Solids content, wt-% in:		
Feed liquor	45	44
Product liquor	59	54
Second critical solids, wt-%[2]	57	53

[1]Effect with most severe fouling
[2]Calculated using NAELS

The black liquors from both mills A and B had high Na_2CO_3 levels. Figure 1 shows that, by reducing the Na_2CO_3 concentration in the liquor, both the first and second critical solids points are moved to higher values. Changes have been made at Mill A to reduce the Na_2CO_3 level. Soluble scale fouling in the first effect has been reduced as a result of this and other actions. No results have as yet been reported to us from Mill B.

Figure 2 show what happens when precipitator catch is added to the recirculating liquor in a falling-film LTV that had been operating with its feed and product liquor concentrations on either side of the second critical solids point of the liquor. The first critical solids moves to a lower value, but the second critical solids point increases. Addition of precipitator catch to the recirculating liquor at this point would also provide more surface area for sodium salts to precipitate on, further reducing scale deposition.

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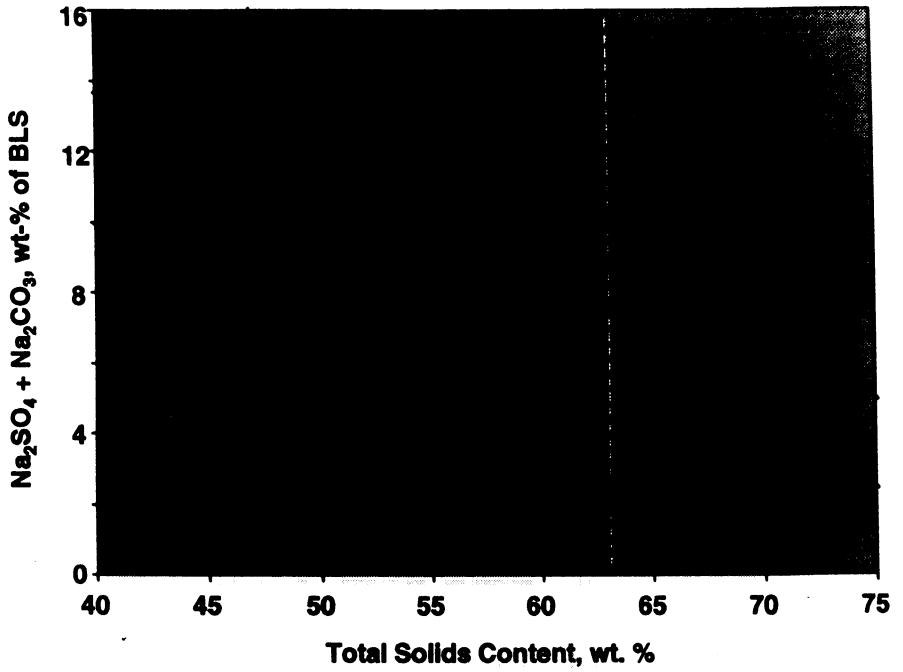

Figure 1. How reducing the Na_2CO_3 content of a black liquor changes its first and second critical solids points.

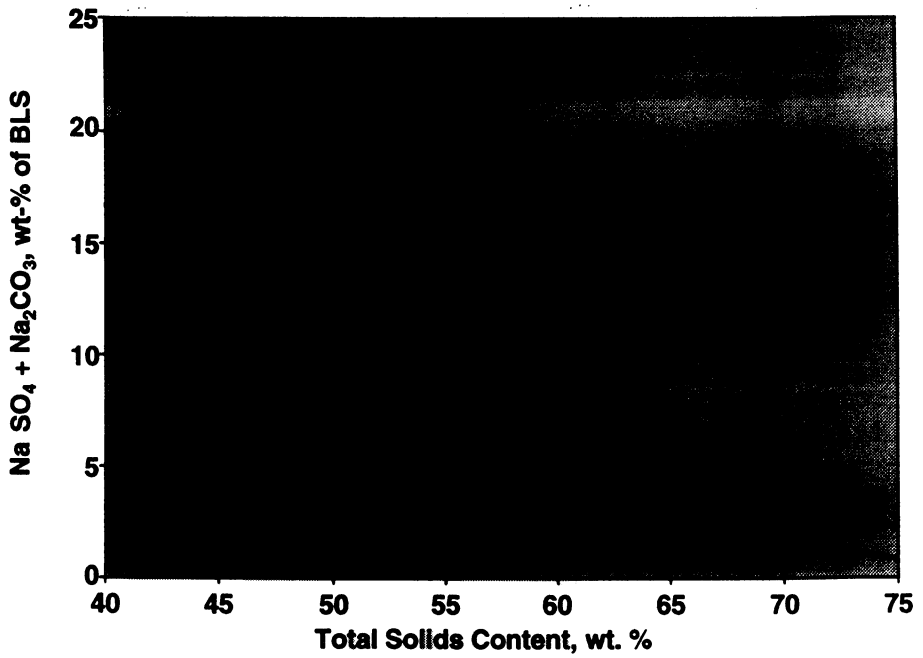

Figure 2. How adding precipitator catch to a black liquor of a black liquor changes its first and second critical solids points.

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2. Summary of Sodium Salt Solubility Data

Aqueous Systems

Since the previous pack meeting, improvements have been made to the systems with tests being done to confirm the quality of the modifications.

Further experiments have been done with aqueous systems pertinent to the burkeite system, including some initial work with potassium carbonate. These, when completed, will be used to further tune the temperature dependency for the solubility of sodium and potassium compounds.

The systems in which work has been done in the greatest detail are: Na_2CO_3-Na_2SO_4-H_2O and Na_2CO_3-Na_2SO_4-NaOH. They have been studied at temperatures of 120°C and 140°C. For the burkeite system an initial test has been run to 160°C. Work with the K_2CO_3-Na_2CO_3-NaOH system has begun.

Work with aqueous systems will continue and include systems involving Na_2S, NaCl, Na_2SO_3 and $Na_2S_2O_3$.

The tests are focused on compositions relevant to the liquor systems in the recovery cycle.

Black Liquor

Two runs to determine the dissolution rate in 45% black liquor at 98°C have been made. The initial run indicates 60% of equilibrium is reached within 40 minutes after addition while equilibrium is reached in approximately 24 hours. The second run was done with multiple samples pulled in the first hour to establish a formula for the dissolution rate.

This test was run by bringing a liter of black liquor to 100 °C, opening the vessel and adding a known amount of precipitator ash. This was done in a stirred, heated pressure vessel with perfect mixing. Enough precipitator ash was added to bring the total solids to 51%. This is above the calculated first critical solids point to ensure an equilibrium point was obtainable.

This study was done to help shed some light on the effect of precipitator ash addition prior to the concentrators in non-pressurized systems.

Difficulties in eliminating carry-over during the concentration period have delayed studies at higher solids but modifications to two systems should allow us to begin method development for establishing the second critical solids point.

GOALS FOR FY 98-99:

A. Experimental Scaling Studies

1. Complete the solubility measurements for sodium salts in black liquor at high total solids concentrations.
2. Obtain on-line crystal size distribution measurement equipment.
3. Conduct pilot-scale evaporator tests to determine the relationship between evaporation rate, liquor recirculation rate, soluble scale deposition rate, and concentration and size distribution of the suspended inorganic particles.
4. From (2), define bounds for heat flux, liquor recirculation rate, and particle concentration for minimal fouling in falling film evaporators.

B. Survey of Evaporator Fouling

1. Issue the final report.

C. Modeling of Sodium Salt Solubility in Black Liquor

1. Collect liquor composition data from mills industry-wide with soluble scale problems in one or more effects of falling film evaporators and concentrators. Calculate the second critical solids point for each case to see how well the second critical solids point correlates with soluble scaling in these units.

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2. Evaluate the NAELS model with the solubility data from A.1. Update the Na-organic interaction parameters in the model as needed.

DELIVERABLES:

1. The final report on the results from the evaporator fouling survey.
2. A brief report summarizing the comparison of calculated second critical solids points with soluble scaling experience in falling-film evaporators.
3. An interim report on the pilot-scale evaporator experiments (from A.3).
4. Experimental data on the solubility of sodium salts in black liquor at high total solids concentrations.

SCHEDULE

Please see the Gantt chart on the following page.

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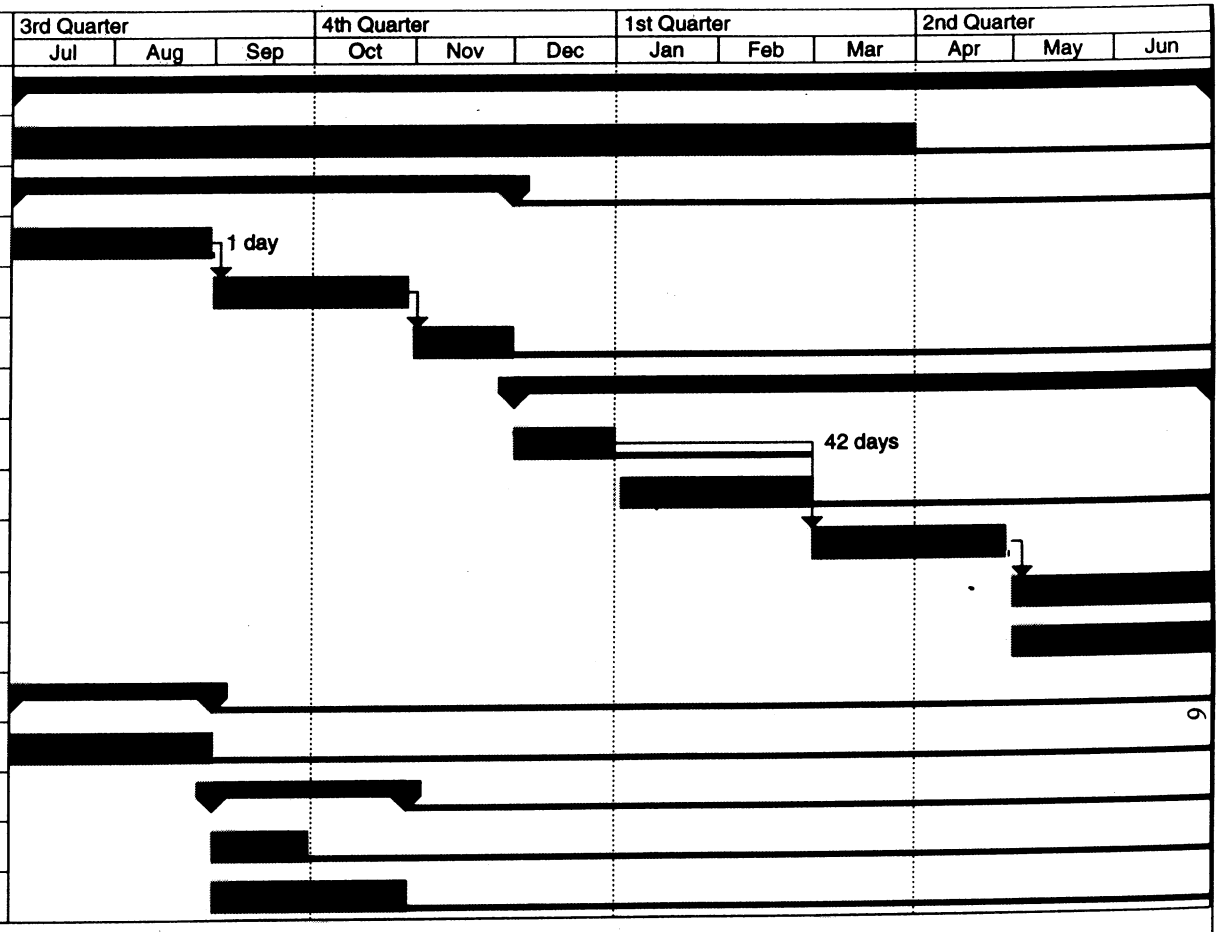
ID	Task Name
1	**A. Experimental Scaling Studies**
2	1. Solubility measurements in black liquor
3	**2. On-line crystal size dist. meas. eqp.**
4	a. obtain funds
5	b. purchase
6	c. Install and start up
7	**3. Pilot evaporator tests: impact of**
8	a. evaporation rate
9	b. liquor recirculation rate
10	c. suspended particle concentration
11	d. size distribution of particles.
12	4. define opn limits for FFE's
13	**B. Survey of Evaporator Fouling**
14	1. Issue the final report.
15	**C. Model Sodium Salt Solubility in Black Liquor**
16	1. Compare 2nd crit solids with FFE scale experience
17	2. Evaluate, update NAELS, OLI models



Project: F017-04 Gantt FY00
Date: Thu 3/18/99

Critical Task
Critical Split
Task
Split
Progress
Milestone
Slack
Slippage
Summary
Rolled Up Critical Task
Rolled Up Critical Split
Rolled Up Task
Rolled Up Split
Rolled Up Milestone
Rolled Up Progress
External Tasks
Project Summary

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DUES-FUNDED PROJECT SUMMARY

Project Title:	Control of Non-Process Elements in Kraft Pulp Mills and Bleach Plants
Project Code:	
Project Number:	F017-04
PAC:	Chemical Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	J. Frederick, W. Schmidl, A. Rudie
Staff:	
FY 98-99 Budget:	$86,619
Allocated as Matching Funds:	$12,847
Time Allocation	
Faculty/Senior Staff:	J. Frederick (3%), W. Schmidl (50%), A. Rudie (-)
Support:	M. Amundsen (25%)
Supporting Research	
M.S. Students:	None
Ph.D. Students:	None
External:	G. Rorrer, M. Laver, W. Yantasee, D. Ming, Oregon State University

RESEARCH LINE/ROADMAP: Environmental Performance. 4. Reduce water usage in Bleached Kraft Pulp production to 2500 gallons per ton.

PROJECT OBJECTIVES:

The objective is to provide the pulp and paper industry with an equilibrium calculator capable of handling accurately dissolved inorganic ions, their complexation behavior with organic matter, their adsorption on wood pulp fibers, and inorganic precipitates. The simulator should be compatible and interfaceable with the major process simulators used by the pulp and paper industry.

PROJECT BACKGROUND:

Non-process elements are becoming a major problem in both kraft pulp mills and bleach plants as water use is reduced. A limiting factor for these mills is that there is currently no way to predict accurately the level to which critical elements such as Al, Cl. Fe, K, Mg, Mn, Si, and other metals will accumulate as chemical cycles are closed more tightly. The process simulation tools available lack the capability for predicting the equilibrium distribution of these elements between inorganic ions, dissolved organometal complexes, ions adsorbed on wood pulp fibers, and inorganic precipitates.

Work in this area was begun in 1994 by IPST, and in 1996 by Oregon State University under the DOE/Agenda 2020 program. These programs were brought together when Jim Frederick moved from OSU to IPST. FY99 will be the final year of the OSU work under DOE/Agenda 2020.

SUMMARY OF RESULTS:

The results to date for FY99 are presented by goal from the FY98 report.

1. Measurement of stability constants for wood organics with metal ions.

   This has turned out to be the most difficult part of the entire project, and a significant amount of work has gone into development of experimental methods. The main reason is that standard chemical

indicator-based methods have not worked well because the indicators form much stronger complexes with metal ions than do black liquor organics.

In spite of these difficulties, some data has been obtained. The stability constants obtained for Mg binding to black liquor organic matter are from 1300 to 18,000 (log(K) = 3.1 to 4.3) at pH 10, and 16,000 to 46,000 (log(K) = 4.2 to 4.7) at pH 11. For Ca, a value of 12,000 ((log(K) = 4.1) This last value agrees reasonably well with Westervelt's value of 5000 (log(K) = 3.7) for calcium binding to a lignin model compound.

The number of complexing sites in lignin from kraft black liquor was determined by precipitation of a lignin sample from alkaline solution with barium. A value of 0.0016 moles of monovalent sites per gram lignin was obtained.

2. Correlate stability constants with chemical properties of organic matter.

   Stability constants for various metal ions with carboxylic acid and hydroxyl groups on organic molecules similar to those derived from pulping and bleaching of wood were obtained from the literature. These data showed that the stability constants for metal cations with phenolic hydroxyl groups are two to seven orders of magnitude greater than with aliphatic hydroxyls or carboxylic acids, or with phenolic carboxylic acids. Further, guaicyl type structures account for about 85% of the phenolic hydroxyl groups in the wood degradation products from pulping and bleaching. The following are stability constants at 25°C, obtained from the literature for metal cations binding with guaicyl type structures. The more limited heat of formation data is used to estimate the stability constants at other temperatures. Values in the range shown are typical. The temperature effect can be important: the stabiity constant for cobalt decreases by a factor of 11 from 25°C to 75°C, while the stability constant for hydrogen ion decreases by a factor of 4.

Table 1. Stability constants for protons and metal cations with guaicyl type structures.

Ion	log $K_{M,25}$	ΔH, kJ/mole
H^+	10.0	-23.4
Na^+	0.7	
Ca^{2+}	3.7	0
Co^{2+}	8.6	
Cu^{2+}	13.9	-41.9
Mg^{2+}	5.7	
Mn^{2+}	7.7	
Ni^{2+}	8.9	
Fe^{3+}	8.0	

3. Correlation of adsorption parameters with functional group content of fibers.

   This work is in progress and will be completed by June.

4. Complete the evaluation of the inorganic database.

   Additional metal ion concentration data (see Table 2, below) were therefore obtained from a Georgia kraft pulp mill for comparison with predicted equilibrium concentrations of Ba, Ca, Mg, and Mn in green and white liquors. The results are included in Table 2 (see results for goal 6, below). For the filtered liquors, the concentrations of Ba, Ca, and Mn were usually below the detection limit. In those cases where they were not (table 1 data in **bold**), the data show that hot versus cold filtering can make a difference, but not by as much as an order of magnitude. The Ba concentration for the one sample above the detection limit (Clear – Hot green liquor) is close to the predicted value. The Ca

concentrations in white liquor are a factor of 3-4 above the predicted values. The predictions for Mn are $10^3 - 10^4$ times lower than the measured values. These results are not substantially different than our earlier comparison between Bryant's data and the predictions, and our earlier conclusions have not changed. Additional work is needed to determine why the calculated results for Mg and Mn agree so poorly with the experimental data.

5. Develop an organo-metal equilibrium calculator.

   A preliminary model was developed, and calculations were made for a brown stock washer to evaluate it. The model is based on experimental adsorption data, the stability constants described in Table 1 (above) and the OLI chemical equilibrium simulator. The OLI software has simple flowsheeting and mass and energy balance capabilities. A 2-stage brownstock washer model was simulated using split and mix blocks. With this model, it was possible to compute the metal partitioning between pulp fibers and solution in a two-stage drum washer process. The simulator accounted for the distribution of metals between soluble inorganic species, soluble organometal complexes, metals adsorbed on fibers, and inorganic precipitates. The simulation results were compared to data reported earlier by Bryant. Reasonable agreement was obtained.

   An important result of this preliminary study is that most of the metals entering the brownstock washers remain as inorganic precipitates throughout the washers. These precipitates most likely remain with the fibers rather than with the wash liquors. If so, most of the metals would go with the fibers to the bleach plant, and not be transported with the black liquor and purged as dregs. Also, metals that enter the brownstock washers with recycled bleach filtrate will be returned to the bleach plant. This would result in increased metals build-up in the bleach plant.

6. Obtain additional data for mill liquor, bleach filtrates, and pulp streams.

   Last year we had reported that we had found quite variable agreement between predicted concentrations of multivalent cations in green and white liquors with data from mill liquors. The mill liquors had been sampled, brought back to IPST, stored, and analyzed sometime later. We suspected that the concentrations of these cations may have changed upon cooling. A new sampling and analysis study was therefore completed to determine if filtering of the samples while hot versus after cooling made a difference in the measured soluble metal content.

   In this study, samples of green and white liquors were obtained from a Georgia kraft pulp mill. The samples taken and collection points were as follows:

   - Raw green liquor: clarifier feed transfer pump.
   - Clear green liquor: slaker feed transfer pump.
   - Raw white liquor: causticizer stand pipe transfer pump.
   - Clear white liquor: digester feed, swing storage tank transfer pump.

   The raw liquor samples were filtered immediately through a 0.45μm PTFE membrane. They are labeled "Raw – Hot" in Table 2. The clarified liquor samples were filtered a 0.45μm Nylon membrane. They are labeled "Clear – Hot" in Table 2. Other samples were cold filtered later at IPST through a 0.45μm membrane filter. They are labeled either "Raw – Cold" or "Clear – Cold" in Table 2. These samples plus the unfiltered raw and clear liquor samples were analyzed for Ba, Ca, Mg, and Mn content.

7. Predict the solubility limits of metals in mill liquor and bleach filtrate streams.

   See items 4 and 5, above.

8. Evaluate the estimation procedure.

   See items 4 and 5, above.

9. Write final DOE report.

   This will be completed by the end of July.

Table 2. Measured and predicted concentrations of Ba, Ca, Mg, and Mn in green and white liquors.

Analyte	Bryant[1]		Results from this study: liquors from one kraft mill					Simulated
Green Liq.	Clear - Cold	Total	Raw - Hot	Raw - Cold	Total	Clear - Hot	Clear - Cold	Hot
Ba, mg/kg	1.5 – 2.9	<1.2	<1.3	<1.3	**1.4**	**1.7**	<1.3	1.3
Ca, mg/kg	15 – 21	**178**	<13	<13	<13	<13	<13	1.1
Mg, mg/kg	1.9 – 5.8	**26**	<11	<11	<11	<11	<11	$3x10^{-4}$
Mn, mg/kg	1.6 – 3.1	**15**	**2.50**	**0.57**	**2.5**	**1.6**	**0.38**	$7x10^{-4}$
White Liq.	Clear - Cold	Total	Raw - Hot	Raw - Cold	Total	Clear - Hot	Clear - Cold	Hot
Ba, mg/kg	0.3 - 0.8	**3.1**	<1.3	<1.3	<1.3	<1.2	<1.3	1.4
Ca, mg/kg	9.7 - 85	**26,600**	<13	**20**	**42**	**18**	**14**	4.8
Mg, mg/kg	1.7 – 2.9	**472**	<11	<11	<11	<9.9	<11	$3x10^{-6}$
Mn, mg/kg	1.8 – 3.1	**9.1**	**0.34**	**0.41**	**2.6**	**0.51**	**0.40**	$2x10^{-5}$

[1]Earlier IPST study. Range is for 3 mills)

GOALS FOR FY 00:

1. Identify an industrial partner, whose brownstock washers and bleach plants will be the subject of this study, and technical experts from that company who will participate in this project.
2. Develop and validate steady-state mass and energy balance models for the brownstock washers and bleach plant of the kraft pulp mill involved.
3. Implement the models to develop strategies for managing metals and oxalate in the brownstock washers and bleach plant of the mill.
4. Conduct mill trials to evaluate the strategies developed.

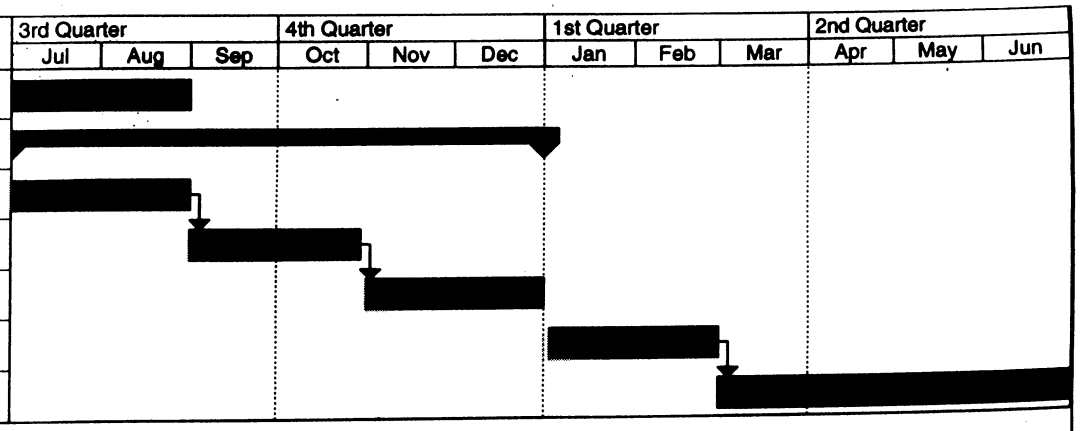
DELIVERABLES:

1. An advanced, validated simulation capability for developing and evaluating strategies for managing metals and oxalate in kraft pulp mills and bleach plants, and scales in bleach plants.
2. Documented demonstration of the simulation capability for developing and evaluating strategies for managing metals and oxalate in kraft pulp mills and bleach plants, and scales in bleach plants.
3. Guidelines for managing metals and oxalate in kraft pulp mills and bleach plants, and scales in bleach plants.

SCHEDULE:

(See following page)

ID	Task Name
1	1. Identify an industrial partner
2	2. Brownstock washer/bleach plant models
3	a. input/evaluate OLI software's oxalate parameters
4	b. Develop steady-state mass and energy balance models
5	c. validate steady-state mass and energy balance models
6	3. Develop strategies for managing metals and oxalate
7	4. Conduct mill trials to evaluate the strategies developed



Project: F01704a Gantt FY00
Date: Thu 3/18/99

Task
Split
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Split
Rolled Up Milestone
Rolled Up Progress
External Tasks
Project Summary

Confidential Information - Not for Public Disclosure
(For IPST Member Company's Internal Use Only)

DUES-FUNDED PROJECT SUMMARY

Project Title:	Closed Mill Salt Recovery
Project Code:	
Project Number:	F01706
PAC:	Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	P. Pfromm
Staff:	D. Taylor (Senior Technician)
FY 99 Budget:	July 98 to June 99: Budget $129,822
Time Allocation	
Faculty/Senior Staff:	P. Pfromm: 35%
Support:	D. Taylor: 75%
Supporting Research	
M.S. Students:	-
Ph.D. Students:	E. James Watkins
External:	None

RESEARCH LINE/ROADMAP: Environmental Performance 4. Reduce Water Usage in Bleached Kraft Pulp production to 2500 gallons per ton.

PROJECT OBJECTIVE:

Evaluation of selective removal of chloride and potassium from low-effluent kraft pulping by electrodialysis of dissolved electrostatic precipitator catch (ESP catch) is the purpose of this project. Concentrations in the liquor streams can then be controlled to avoid corrosion and recovery boiler plugging.

PROJECT BACKGROUND:

RAC recommended area I, as of 11-16-1994, "Minimize the Environmental Impact"

Subgoal: Develop separation technologies for Non Process Elements (NPE's).

Subtask d: Eliminate unwanted chlorine compounds (no end-of-pipe).

The removal of chloride from the kraft pulping operation is necessary due to the negative impact of increased chloride concentrations on recovery boiler operation (sticky deposits), and corrosion. One method of chloride control is to discard large amounts of the ESP catch. On the other hand, if the chloride could be removed selectively, the ESP catch could be recycled, resulting in a direct payback due to savings in chemical makeup. In addition, the inorganics discharged to waste treatment and to the environment would be very significantly reduced.

Currently, crystallization of an ESP catch slurry is being tested by Champion International for chloride and potassium control. The simplicity of the membrane process proposed here, in

addition to ease of operation and low energy demand are the motivation to explore this technology.

The chloride purge stream from crystallization will contain organics. That is not the case for electrodialysis, where all organics are recycled with the saltcake to the recovery boiler, and a purely inorganic salt solution is discharged.

The total chloride removal capacity from the ESP catch by any technique may not be sufficient for some bleach plant closure schemes. If proven feasible for actual ESP catch in presence of organics, electrodialysis for chloride control could be used in the bleach plant. This is not directly possible for evaporation/crystallization.

BENEFITS

The benefits of selective chloride removal from the ESP catch by electrodialysis are:

- Reduced chemical makeup (direct payback)
- Reduced environmental impact
- Reduced washing frequency for the recovery boiler (increased productivity)
- Reduced corrosion

The advantages of electrodialysis vs. alternative processes (evaporation/crystallization, ion exchange) are:

- Continuous process
- No organics entrained in the chloride purge
- No regeneration chemicals needed
- Simple startup/shutdown
- Chloride removal rate is easily adjusted
- Low energy requirements
- Low space requirements

SUMMARY OF OBJECTIVES VS. RESULTS, PROPOSED BY P. PFROMM AT SPRING 1998 PAC

Objective A:
Technology transfer, electrodialysis of ESP dust
A1. Continue work with US Filter/HPD for full scale application
US Filter/HPD confirmed per Gerald Delaney that engineering and implementation could be done by HPD, but that no warranty on the lifetime of membranes would be available, since HPD does not manufacture them.

A2. Address recycling of sulfate rich solution.
The attempt to reduce the water load further is reported below.

A3. Further pilot scale tests if financial support from a host mill is supplied (lease/transport unit, on site support, support for analytical services). IPST's membranes would be used.
No financial support for further pilot tests was obtained.

Objective B:
K/Na selective membrane separation:
B1. Run K/Na sulfate mixture with conventional membranes to obtain baseline for K/Na selectivity.
The results from the long term high concentration experiments will be reported below, or at the PAC meeting as available. K/Na separation results should be also available as the analytical data is obtained.

B2. Run composite anion/cation exchange membrane to quantify improvement of K/Na selectivity (anion exchange membrane as a size/charge selective "filter" for cations)
No progress.

B3. Consider new chemistries for K selective membranes (with A. Ragauskas)
Cooperation with an existing project at Pacific Northwest National Laboratory (PNNL) was established. The work at PNNL focused up to now on an inorganic carrier-type membrane. Recently, modifications of existing technical membranes were found to be promising. Discussions on technical issues with PNNL were continued and P. Pfromm is a co-investigator on a pending DOE Agenda 2020 proposal for enhanced selectivity for K/Na of ion exchange membranes.

B4. Test new chemistry initially as resin.
See above, B3.

Objective C:
Ion exchange for combined chloride/potassium removal from green liquor.
Previous work: MS student D. Englehart is completing study on selective potassium removal from green liquor with commercial ion exchange resins.
C1. Literature update
Planned for late FY99.

C2. Select commercial anion exchange resin.
Planned for late FY99.

C3. Bench-scale tests
Planned for late FY99.

RECOMMENDATIONS/FEEDBACK AFTER FALL PAC MEETING 1998

1. Continue efforts for full scale installation at 25+% solids in the feed. Write brief description of economics to aid in finding prospective locations.

See below for economics and high concentration test.

2. Resolve economics
   See below.

3. More work on K/Na separation
   Cooperation initiated with PNNL

SUMMARY OF RECENT RESULTS:

Goal of experiments at high feed concentration

The goal was to perform an extended continuous experiment with actual ESP dust at high feed concentrations. The minimization of adding water to the process for dissolving dust will facilitate integration of electrodialysis into the recovery cycle. A highly concentrated dechlorinated ESP dust slurry could be sent to the concentrator with minimal excess evaporation capacity needed.

The experiment should result in electrical current efficiency data for chloride removal at high solids (ESP dust) concentrations, fouling information, and information on the limiting current density. The results would then be used in the existing process design spreadsheet to obtain operating costs.

Experiments at high feed concentration:

A long term laboratory scale run was performed with ESP dust obtained from a Southeastern Kraft mill. The dust was dissolved in water to 25 weight% of solids for the electrodialysis experiment. The feed solution to the electrodialysis contained on average 4.72 g chloride/liter of solution (3.78 grams chloride per kg of solution) and 158.8 g sulfate/liter of solution (127.24 grams sulfate per kg of solution). The feed solution was not filtered or pre-treated in any way.

The run was performed as a continuous run at a temperature between 39.8°C and 40.3°C with feed-and-bleed operation for both the feed (dissolved ESP dust) and concentrate (purge) streams (see Figure 1). The total membrane area was 300 cm^2 each of cation and anion exchange membrane exposed to the feed stream. Three diluate and three concentrate compartments were installed in the electrodialysis stack.

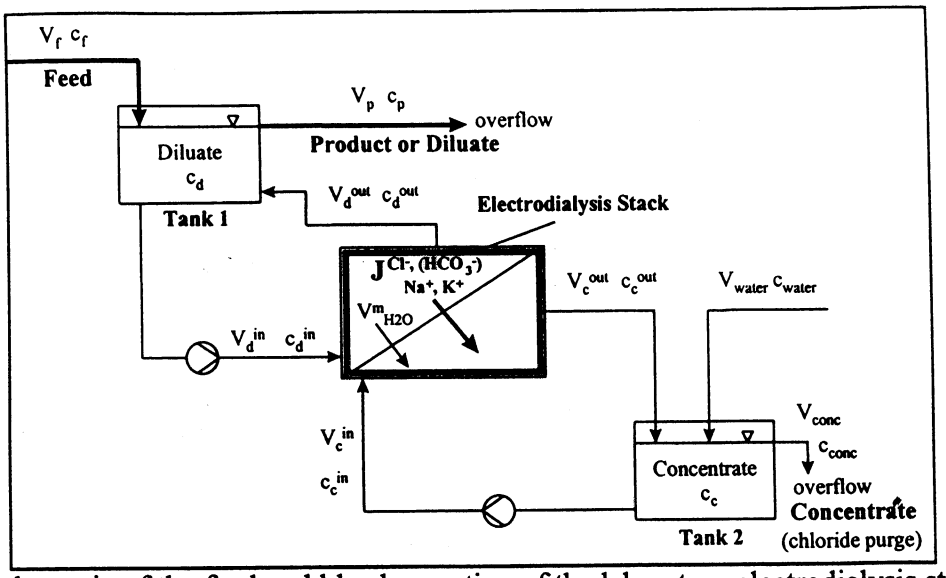


Figure 1: Schematic of the feed and bleed operation of the laboratory electrodialysis stack (V volume flow in l/hr, c concentration in g/l, J mass flow in gram/hr cm^2 membrane area).

The purge (concentrate) stream was initially a 1 mol/liter sodium chloride solution (4 liters), to allow for a faster approach to overall steady state operation. The feed (diluate) was started with 4 liters of the dissolved ESP dust solution. In an initial batch portion of the run, the feed chloride concentration was lowered to approach the equilibrium level that was predicted for the entire feed-and-bleed portion of the run.

Table 1: Parameters for a high feed concentration continuous laboratory feed and bleed run (see Figure 1 for parameters). Run duration 68.8 hours.

Parameter (see Figure 1 also)	Value
V_f	1.36 liters/hour average
C_f, chloride	4.72 gram/liter
C_f, sulfate	155.8 gram/liter
C_p, chloride	2.65 gram/liter average
Average chloride removal from feed	44 %
V_{water}	0.064 liters/hour average
C_{conc}, chloride	34.27 gram/liter
C_{conc}, sulfate	1.52 gram/liter
V_d^{in} Recirculation rate Diluate	152 liters/hour
V_C^{in} Recirculation rate Concentrate	186 liters/hour
Electrical current	0.7 Ampere, 7 mA/cm^2
Total stack voltage	3.3-3.7 volts
Voltage per cell pair (1 dil.+1 conc. compartment)	1.1-1.23 volts

The average chloride removal was relatively low (44%). The electrodialysis parameters were calculated before the run to remove 70% of the chloride from the feed. However, this was based on an analysis of the dry ESP dust chloride content. When analyzing the feed solution

made by dissolving this dust, it was found later that the feed chloride concentration was much higher than expected, probably due to an incorrect initial analysis of the dry dust. Therefore, the design (70% chloride removal level) was not reached since the feed chloride content was higher than expected. To achieve 70% chloride removal the electrical current should have been set at 1.1 amps, rather than the 0.7 amps that were used.

Figure 2 shows the chloride and sulfate concentrations in the feed and purge tanks of the electrodialysis stack as a function of time during the experiment. It is apparent that the run showed reasonable steady state behavior, within the limits of fluctuations in the feed-and-bleed volume flow rates.

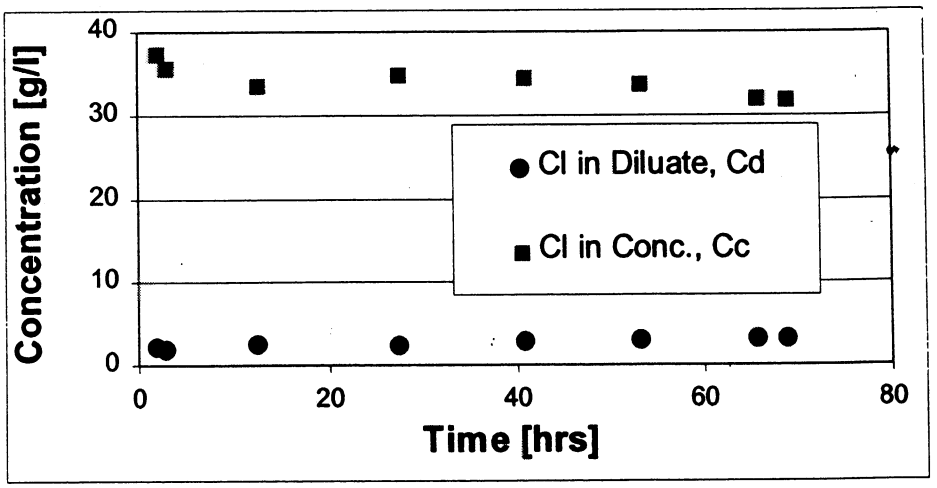


Figure 2: Chloride concentration in the diluate overflow V_p (dechlorinated ESP dust solution) and concentrate overflow V_{conc} (purge stream) during feed-and-bleed electrodialytic dechlorination of a 25wt% ESP dust solution.

Figure 3 demonstrates the selectivity of the process towards chloride transport. Despite the very high sulfate concentration in the feed (diluate), only very little sulfate leakage to the concentrate occurs. The sulfate is retained to a very high degree, while the chloride is removed.

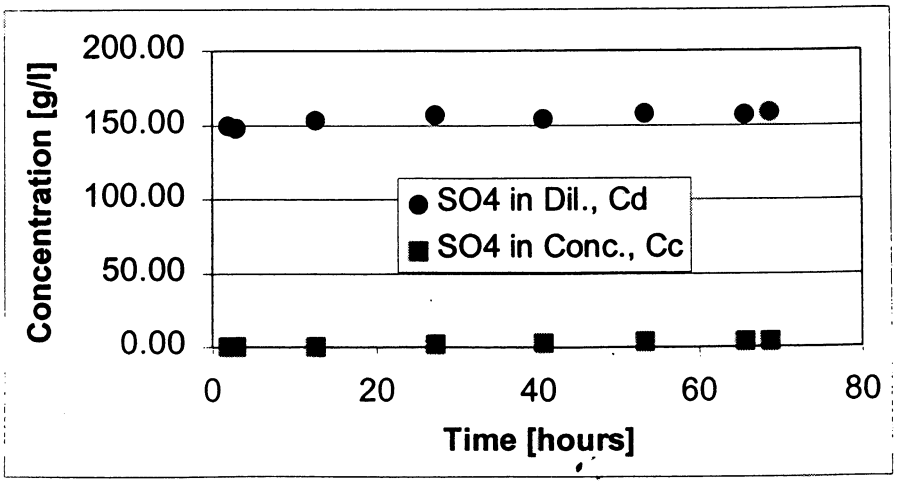


Figure 3: Sulfate concentration in the diluate overflow V_p (dechlorinated ESP dust solution) and concentrate overflow V_{conc} (purge stream) during feed-and-bleed electrodialytic dechlorination of a 25wt% ESP dust solution.

At 100% current efficiency for the transport of chloride from the diluate to the concentrate, 5.5 mol of chloride would have been removed from the diluate. From analysis of the diluate overflow, 5.5 mol of chloride were removed. This would equal an unrealistic 100% current efficiency. Calculating using the concentrate analysis, a total of 4.3 mol of chloride was received from the diluate. The discrepancy between chloride removal from diluate and chloride appearing in the concentrate is likely due to fluctuations in the feed-and-bleed rates, and analytical inaccuracies.

It was attempted to determine the limiting current density for this feed. However, the limiting current density experiment (stepwise increase of the current, until electrical losses by water splitting become apparent) was not conclusive. No inflection point was observed

Conclusion of experimental results

In summary, electrodialysis of dissolved ESP dust can be performed without significant problems. The dust was easily dissolved in water at 25wt% of solids by stirring, and was not pre-treated in any way before electrodialysis. A long term laboratory scale experiment of 68.8 hours in the feed and bleed mode showed essentially constant process performance.

DESCRIPTION OF OPERATING COSTS AND CAPITAL INVESTMENT FOR THE TECHNOLOGY

A typical installation is outlined below. The results are based on an Excel design spreadsheet developed during this project.

Assumptions:

- 1000 kilogram of chloride to be purged per day
- Chloride content of the solid ESP dust is 1.5wt%
- ESP dust will be slurried up to 316 grams of solids per liter.
- Removal of 70% of the chloride from the dust slurry in a feed-and-bleed electrodialysis system.
- Limiting electrical current density for the electrodialysis is 12 mA/cm^2
- Electrical current efficiency is 70% for chloride (70% of the electrical current applied will successfully remove chloride)

Resulting process parameters:

- 96 metric tons of dust (containing 1,400 kilograms of chloride) need to be dissolved and treated per day. About the same amount is recycled to the evaporators or the concentrator after removing the chloride.
- 55.6 gallons of water per minute (80,000 gallons per day) will be used to dissolve the dust and must be evaporated for recycling.
- The membrane area is 350 m^2

Operating costs

- Energy costs for electrodialysis, pumping: $25,000/year

- Energy costs of evaporation of water from recycled slurry in sextuple-effect evaporator train: $160,000/year
- Assume a membrane lifetime of 2 years: $72,600/year for replacement membrane cos

Capital costs

Based on a previous quotation form a manufacturer of electrodialysis equipment, the capital costs for the electrodialysis unit only, including recirculation pumps and tanks, would be on the order of $500,000 to $800,000. This excludes all capital needed to modify or add equipment besides the electrodialysis unit, for example dust slurrying and transfer.

Annual savings, payback

The savings are based on comparing discarding of whole ESP dust (and replacing the lost sodium sulfate by purchasing on the market) versus selectively removing the chloride and recycling the ESP dust. Using a cost of $114 per ton of saltcake, and including the operating costs above, savings of about $1,800,000 per year would be realized, resulting in a payback of on the order of less than one year.

HIGHLIGHTS OF MS RESEARCH REPORT FOR ION EXCHANGE OF GREEN LIQUOR TO REMOVE POTASSIUM FORM THE KRAFT PULPING CYCLE

The PAC had previously requested a summary of this work. Artificial green liquor was treated by percolating it through a laboratory scale ion exchange column containing a commercial cation exchange resin loaded with sodium. Potassium from the liquor would enter the resin, and sodium would be released from the resin. The separation factor K based on the K and Na concentrations in the resin and in the solution at equilibrium ($K=(K_{resin}\ Na_{solution})/(Na_{resin}\ K_{solution})$) for artificial green liquor with a K/(K+Na) ratio of 0.07 (similar to current mill conditions) was about 9, indicating good potassium selectivity.

Scaleup calculations showed that a 100 ft^3 bed of the ion exchange resin (resin costs total $10,000) will be sufficient to remove 1100 kg of potassium per day from green liquor in only 10 load/regeneration cycles per day. This would balance the potassium input of a pulp mill with about 1000 AD ton of pulp produced per day.

Regeneration of the ion exchanger could be done with caustic, and the potassium rich effluent could be discarded or used downstream from the pulp mill (perhaps in the bleach plant). Alternatively, sulfuric acid or another acid could be used for regeneration, and the resin could be loaded with sodium using sodium sulfate after the potassium has been removed by the acid.

To complete this process, chloride removal with commercial ion exchange resins could be investigated. Even small selectivities of chloride over other anions (especially hydrosulfide and hydroxide) would suffice to use ion exchange resins for chloride control, due to the low cost of ion exchange, and the well-proven and rugged process.

Ion exchange of green liquor has another very significant advantage over all other processes suggested for chloride and potassium control: all potassium and chloride is available

for removal, not just a side stream. In addition, no water needs to be evaporated to run the process.

GOALS FOR IPST FY 2000 (JUNE 1999 TO MAY 2000):

Project F01706 will be terminated with the end of FY 1999 (June 1999). Contacts with mill personnel and member companies interested in chloride removal by electrodialysis will continue as needed. If an opportunity for a full scale installation arises, potentially with DOE support, proposals will be developed under IPST's proposal program, and the PAC will be consulted.

DELIVERABLES: FINAL MEMBER REPORT (REPORT NUMBER 4)

Highlights of Externally Funded and PhD Projects

DOE FUNDED PROJECT

Sponsor: DOE Agenda 2020, Energy Performance Task Group

Project Title:	Elimination of the calcium cycle: direct electrolytic causticizing of Kraft smelt
Project Code:	
Project Number:	4182
PAC:	Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	P. Pfromm, J. Winnick (Georgia Tech)
IPST Staff:	D. Taylor (Senior Technician); Research Services Division
FY 99 Budget:	August 97 to October 98 (1 year project, 2 month no cost extension): $180,000 total
Time Allocation	PROJECT ENDED 10-98
Faculty/Senior Staff:	P. Pfromm, J. Winnick, ~1 month each (Pfromm from IPST matching funds)
Support:	D. Taylor: 12.5%
Supporting Research	
M.S. Students:	
Ph.D. Students:	R. Wartena (Georgia Tech)
External:	This project is external

RESEARCH LINE/ROADMAP:

Project Objective

Show on the laboratory scale that electrolysis of a sodium sulfide/sodium carbonate salt smelt in presence of steam at the cathode and a sacrificial carbon anode will result in causticizing of the smelt without any significant sulfur loss:

Original proposal:
1. production of hydroxide and hydrogen from steam at the cathode
2. release of carbonate as carbon dioxide at the cathode

Actual result of the feasibility study:
Alternative process, no steam injection at cathode: formation of sodium oxide in the smelt, release of carbonate as CO2.

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Project Background

The Gibbs free energy change was calculated at 1100 K. It is clear that formation of CO_2 from $CO_3^=$ at the carbon anode is the expected reaction. This is **only** the case with the sacrificial carbon anode.

Literature search: No references to direct electrolytical causticizing of a kraft molten salt smelt were discovered in the patent literature and the general published literature. Causticizing of carbonate molten salt smelts (no sulfur compounds) has been described. Causticizing of green liquor by electrolysis has also been described, but suffers from the need to first separate the sulfide entirely from the carbonate (for example U.S. Pat. 2,416,413). Our use of steam at the cathode and a sacrificial carbon anode for kraft smelt electrolysis constitutes an entirely novel approach.

Prior or current funding: this work was cost shared at 20% through personnel costs by the Institute of Paper Science and Technology and Georgia Tech.

Benefits to the Industry

The potential benefits are:

- about 50% energy savings over current kraft causticizing
- reduce deadload (unlimited causticizing efficiency, no chemical equilibrium limitation)
- eliminate non-process element input from lime
- facilitate process control (no large dead times)
- incremental causticizing capacity can be installed
- electrolytical unit with about five square meters of electrode area may suffice for a 1000 tpd kraft mill

Since a very similar process exists on a large scale in aluminum production, the technology transfer would be relatively simple, once a proof-of-concept has been established. This feasibility test is the subject of this work.

Summary of Results 8-97 TO 10-99 (end of project)

Feasibility was successfully shown. At the time of this report, a DOE Agenda 2020 proposal is pending (Energy Efficiency Task Group) for funding starting July 1999.

An amount of $100,000 for FY 2000 has apparently been approved by the RAC for this project..

The patent application has been submitted. No doe funded work or results are included in the patent application.

Future of the project

In case no DOE funding is obtained, $100,000 for FY 2000 (apparently approved by RAC) would be used to continue experimental work, involving the Georgia Tech PhD student in Professor Winnick's group.

In case DOE funding is obtained, about $36,000 per year of the above $100,000 would be used as IPST's matching funds as salary for P. Pfromm. DOE funding would allow a much stronger effort by adding a post doc. More materials would be screened, and the hardware would be upgraded (gas sensors, power booster).

Deliverables, FY 2000, IPST member consortium funding only

- Electrochemical studies (cyclic voltammetry) to determine reaction mechanisms
- Test electrode materials and materials of construction
- Test and optimize process conditions and hardware

Highlights of Externally Funded and PhD Projects

DOE FUNDED PROJECT

Sponsor: DOE Agenda 2020, Environmental Performance Task Group

Project Title:	VOC Control in Kraft Mills, Task B: Development of a Membrane Separation Technology
Project Code:	
Project Number:	415702
PAC:	Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	P. Pfromm, M. Rezac (GIT)
IPST Staff:	D. Taylor (Senior Technician); I. Christ (MS student)
FY 98-99 Budget:	~$50,000/year, project ends July 1999
Time Allocation	
Faculty/Senior Staff:	P. Pfromm, 1 month/year (Matching)
Support:	IPST MS Student, GIT PhD students, D. Taylor: 12.5%
Supporting Research	
External:	This project is external

RESEARCH LINE/ROADMAP:

Project Objective

Show on the laboratory scale that methanol can be selectively removed from wet air streams by membrane permeation.

Project Background

Legislative pressure and publicized opinion demand measures to minimize emissions. Only operations that will be able to safely comply with current and future regulations will enjoy long term success. Hazardous Air Pollutants (HAP's) have become a focus for reduction of emissions from pulp and paper mills. Methanol has clearly been identified as the major HAP emitted from pulping and papermaking operations.

We propose to use an emerging technology for separation of methanol from gas and vapor streams to minimize emissions from significant point sources, such as tank vents Ohlrogge and Peinemann, 1990). The removal of methanol through membrane permeation is a continuous, simple, and rugged process. Methanol is recovered as a liquid, and no spent adsorbent is generated. No sludge disposal problem is created, as with biological reactors. In lower concentration ranges, the process is more efficient than condensation. Since the methanol is recovered in liquid form, it can be sold, reused, or easily disposed of. This process is currently being implemented in the petroleum industry for recovery of fuel vapors from tank farms and gas stations. The advantages of methanol recovery by membrane technology are shown in Table 1.

	Methanol recovered	*Regenerate/dispose of adsorbent*	*Sludge generated*	*Startup/shutdown procedure*	*Tolerates feed changes*
Membrane Separation	**yes**	**no**	**no**	**simple**	**yes**
Adsorption	possible	yes	no	yes	limited
Bio Reactor	no	no	yes	complex	no

Table 1: Comparison of alternative control methods for methanol emissions.

Benefits to the Industry

- Reduce environmental impact
- Compliance with regulations
- Recover solvent

Summary of Results 8-98 to 1-99:

- Membranes are available for laboratory evaluation.
- Steam purge experiments are continuing on schedule.

Deliverables

- Form laboratory scale high performance composite membranes
- Confirm engineering approach (steam purge), system design.
- Case studies

Schedule:

Mixture measurements during 1998/99.

Highlights of Externally Funded and PhD Projects

DOE FUNDED PROJECT

Sponsor: DOE Agenda 2020, Environmental Performance Task Group

Project Title:	Recycling of Bleach Plant Filtrates using Electrodialysis
Project Code:	
Project Number:	4160
PAC:	Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	S.-P. Tsai (Argonne National Lab), P. Pfromm
IPST Staff:	D. Taylor (Senior Technician); IPST Research Services
FY 98-99 Budget:	August 98 to August 99: Total $200,000, IPST~$50,000 (3 year project, 1997 to 1999)
Time Allocation	
Faculty/Senior Staff:	P. Pfromm, 1 month
Support:	IPST PhD Student, Analytical Services
Supporting Research	
External:	This project is external

RESEARCH LINE/ROADMAP:

Project Objective

The goal of this work is to develop electrodialysis technologies that will enable the pulp mills to tighten the water cycle by using electrodialysis for the selective removal of inorganic NPE's in the bleach plant filtrates for the recovery of filtrates. Electrodialysis is uniquely suited as a selective kidney to remove NPE's from bleach plant effluent, before they reach the recovery cycle. Therefore, the problems caused by accumulation of inorganic NPE's in the pulping cycle and recovery boiler are prevented.

The efforts in this work have been focused on the acidic bleach plant effluent of bleached Kraft pulp mills, because bleached Kraft pulp production is an important segment of the pulp and paper industry and the acidic effluent is where most of the NPE's are present. The major technical hurdles for this process include the membrane selectivity for the NPE's to be removed and the membrane resistance to fouling. In addition to the technical feasibility, the process economics is crucial to the viability of this process.

The objectives of this work are:

•To evaluate the process feasibility, including ion selectivity and organic fouling resistance

•To develop an efficient and economical electrodialysis-based process at the laboratory scale

•To demonstrate the process performance at mill sites

•To transfer the technologies to pulp and paper companies

Electrodialysis Technology

Electrodialysis is a membrane separation technology that uses the permselectivity of ion-exchange membranes and the electric potential driving force to remove, concentrate, or separate ionic species in aqueous streams. The technology was first developed in the 1950's. Currently, successful applications of electrodialysis exist in various processing industries; these applications include:

•Desalination of brackish water

•Production of table salt from sea water

•Chemical, food, and drug processing

•Water and wastewater treatment

•Waste recovery and recycle from industrial wastewater

The scale of commercial systems ranges from vary large (500 million lb/yr) plants for table-salt production to small-scale systems for flavor-extraction in food processing plants.

Electrodialysis separation is achieved by passing the feed and product streams through an electrodialytic stack comprised of alternating cation-exchange and anion-exchange membranes and applying a direct current to a pair of electrodes across the entire set of membranes. Cation exchange membranes are made of a cross-linked polymer with fixed negatively charged function groups, which permit the transport of cations through the membranes while excluding anions from entering the membranes. Similarly, anion-exchange membranes have fixed positively charged groups, which permit the transport of anions and exclude cations. In the presence of an electric field, cations in the feed (diluate) compartment move towards the cathode, cross through the cation-exchange membrane into the concentrate compartment. Their further movement towards the cathode is blocked by the anion-exchange membrane, resulting in accumulation in the concentrate compartment. Similarly, anions move towards the anode from the feed to the concentrate compartment through the anion-exchange membranes. Most of the non-ionic and weakly ionic species stay in the feed stream, although a small amount can move to the concentrate stream by electro-osmosis. Electrodialysis is, thus, an efficient means of separating the inorganic salts from the non-ionic and weakly ionic organic compounds.

Various kinds of ion-exchange membranes are commercially available from several suppliers. Each of the reputable suppliers (e.g., Tokuyama Corp.) carries more than a dozen different types of membranes. The selection of appropriate membranes are essential to meeting technical and economic objectives for a specific application. Some of the factors that are important to consider when selecting membranes include degree of cross-linking, membrane thickness, and ion selectivity. In general thicker membranes and membranes with a higher degree of cross-linking have better mechanical strength but also higher electrical resistance, whereas thinner membranes and membranes with a lower degree of cross-linking have poorer mechanical strength but lower electrical resistance. Ion selectivity can be an important consideration when it is desired to promote the transport of certain ionic species while minimizing the transport of other ionic species. For example, monovalent-selective anion-exchange membranes can be used to permeate chloride ions while rejecting sulfate ions.

For bleach plant filtrate recycle, electrodialysis can potentially be applied in Concept 3.a and Concept 3.c described earlier. Electrodialysis of bleach plant effluent to remove inorganics, including chloride, has been proposed by Eka Nobel (Gransson et al., 1995). However, an extensive pre-treatment for separation of the organic components before electrodialysis was proposed. This leads to high investment and operating costs. The process proposed here will employ membranes that are intrinsically fouling resistant due to special polymer modifications.

Champion International is currently testing the first installation of their BFR™ process at Canton, NC (Caron and Williams, 1996) to remove metals from the acidic filtrate (Concept 3.c). The metal ion removal sequence requires significant pre-treatment, and is still subject to fouling. Electrodialysis is superior since it requires no regeneration cycles, and can tolerate organic foulants if modified membranes are used. Chloride can be removed by electrodialysis at the same time that metal ions are extracted, which prevents chloride from entering the recovery cycle.

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Gleadow, P., Hastings J. B., Schroderus, S., and Warnqvist, B., "Toward Closed-Cycle Kraft: ECF Versus TCF Case Studies", 82nd Annual Meeting, Technical Section, Canadian Pulp and Paper Association (CPPA), page A359, 1996

Gransson, G., Sundblad, B., Landfors J., and Baltsn, H.A., U. S. Patent 5,437,791; 1995

Caron, J. R. and Williams, L. D., "Design and Start-Up of the Bleach-Filtrate Recycle Process", 1996 International Environmental Conference, Proceedings, p. 669 (May 5, 1996; TAPPI Press)

Benefits to the Industry

Develop a rugged low-cost technology for simple retrofit to remove NPE's from bleach effluent to be recycled.

Summary of Results 8-96 to 1-99:

Detailed results are available as an Annual DOE Report on the project. Please contact P. Pfromm for a copy of the report.

Highlights:

Presentations at the TAPPI Environmental Conference and the International Conference for Membranes and Membrane Processes have been accepted. A paper for the Canadian Journal of Chemical Engineering is in review.

A mill visit at a Member mill to coordinate for a future pilot test was very encouraging. The mill personnel gave a preliminary opinion that the pilot test could be performed. Pilot scale equipment from Argonne National Laboratory would be installed at the mill, and removal of metals and chlorides from the D0 stage effluent would be investigated in a long-term test.

During the mill visit potential carryover of chlorine dioxide into the bleach effluent, and thereby into the electrodialysis unit was discussed. Laboratory experiments with chlorine dioxide exposure of membranes will be performed to check on any detrimental effects.

Highlights of Externally Funded and PhD Projects

IPST PhD PROJECT

Project Title:	Removal of Inorganics from Closed-Cycle Papermachine White Water
Project Code:	
Project Number:	
PAC:	Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	P. Pfromm
IPST Staff:	Eric Watkins, PhD Candidate (Graduation 1998/99)
FY 2000 Budget:	N/A

Highlights

Fouling detection of ion exchange membranes by impedance spectroscopy has been performed. The PhD thesis is being written, graduation is expected in Spring 1999. A paper for the Journal of Membrane Science is in review.

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Highlights of Externally Funded and PhD Projects

IPST PhD PROJECT

Project Title: Behavior of Polymeric Toner in Recycling
Project Code:
Project Number:
PAC: Recovery
Division: Chemical Recovery and Corrosion
Project Staff
Faculty/Senior Staff: P. Pfromm
IPST Staff: J. Panek, PhD Candidate
FY 2000 Budget: N/A

Highlights

A presentation at the ACS Annual Meeting was given. The successful thesis defense took place on February 15, 1999.

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Highlights of Externally Funded and PhD Projects

IPST MS PROJECT

Project Title:	Impedance Spectroscopy for On-Line Characterization of Papermaking Furnishes
Project Code:	
Project Number:	
PAC:	Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	P. Pfromm
IPST Staff:	J. Barrett, MS Candidate (Graduation Spring 2000)
FY 2000 Budget:	N/A

Highlights

The hardware for testing of this new sensor for wet end applications is being designed. A DOE Agenda 2020 proposal is pending, where the M.S. student stipend is used as cost share.

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PROPOSED DUES-FUNDED PROJECT SUMMARY

Project Title:	Ultrafiltration of bleach effluent: new approaches for partial closure
Project Code:	
Project Number:	-
PAC:	Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	P. Pfromm
Staff:	D. Taylor (Senior Technician), Post Doc to be hired
FY 99 Budget:	NONE this was a new proposal to RAC

INDUSTRIAL SPONSOR

Eka Chemicals would support this project with $50,000 per year in cash, $50,000 per year in-kind, and free use of Eka's pilot scale ultrafiltration package plant. Eka has already come forward with a donation of $20,000 to move the project forward.

MOTIVATION FOR THE WORK

This proposal deals with an approach to recycle a portion of the alkaline bleach effluent to chemical recovery. The goal is a process that can be retrofitted to existing mills without major changes in the bleach plant while supplying an energy efficient significant reduction in COD and AOX going from the bleach plant to effluent treatment.

Ultrafiltration is proposed here to achieve some volume reduction, and greatly facilitated treatment of the alkaline effluent. A large part of the water in the bleach effluent will pass through the ultrafiltration membrane, taking with it much of the inorganic load (for example chloride), and the easily treated low molecular weight fraction of the organics. This so-called permeate will be routed to effluent treatment.

The concentrated stream retained by the membrane will contain the majority of the high molecular weight organics, which are difficult to treat in conventional effluent treatment. These organics are responsible for a significant portion of the COD. The concentrated stream will be used in brown stock washing, replacing fresh water and/or condensates.

Figure 1 below shows the basic process. This is fundamentally different form the approach used in much of the previous ultrafiltration work on bleach effluent. There, it was often the goal to produce a permeate that could be discharged without further treatment.

The scaleup of ultrafiltration experiments from the laboratory scale to the pilot or full scale is very difficult and contains great uncertainties, since the fluid dynamics are usually not well reproduced. Therefore, field work proposed here will be performed with ultrafiltration modules of commercial size. After performing field tests to gain experience and identify issues, laboratory work is proposed to follow up on the field tests, and gain a fundamental understanding of critical issues (fouling, selectivity towards various organics).

Although this principle of ultrafiltration of bleach effluent is operating on full scale in Scandinavia, it is necessary to investigate effluents from representative North American mills. The composition of bleach effluents depends strongly on operating strategies and the pulped wood. Differences in the bleach effluent composition can cause significant changes in the performance of ultrafiltration.

Funding Situation

A proposal to DOE was unsuccessful. A proposal to the Georgia Consortium is pending. A proposal was written to the Recovery PAC as requested after the Fall 1998 PAC meeting ($100,000 per year from Member Dues). The proposal was forwarded to RAC for decision. At the time of this report, funding at a level of $50,000 from member dues appears to be a potential possibility. With this level, only one pilot test could be sustained, and the project would have a on year time frame. At full funding level ($150,000/year cash), two pilot tests would be performed per project year. The original goal were four tests (hardwood, softwood, with and without O2 delig).

Fundamentals of Dregs Removal

(Project F01707)

PAC Report

By

H. Jeff Empie
Murray Ellis (PAPRO)
Maribeth Amundsen

March 1999

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ABSTRACT

With the paper industry facing the advent of closed cycle operation in its mills, the question arises as to how the anticipated build-up of non-process elements in the liquor cycle is going to be handled in an environmentally acceptable way. This study was undertaken to determine which elements are going to be problematic at elevated concentration levels. The focus was on dregs removal in the green liquor clarification step in the kraft recovery cycle. Laboratory smelts were generated by adding back one non-process element at a time to a representative base composition and heated these to typical smelt bed temperature, green liquors were formed from these smelts, and the settling and filtration rates of the insoluble dregs that were produced were determined. Comparisons of the addback runs with the base case were made. Samples of mill smelt were obtained and subjected to the same procedures. Finally, a companion sample of actual green liquor from the same mill was obtained and its settling/filtration characteristics established. Chemical and physical analysis of the dregs particles and clarified green liquors were obtained for all of the runs made.

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of Mike Buchanan for his chemical analyses of some very difficult samples, David Rothbard for his physical characterization of dregs particles, Garry Heedick for help with the laboratory equipment, and the IPST support staff for numerous critical tasks. The authors also thank the New Zealand Forest Research Institute Ltd. for loaning M. Ellis to IPST for six months and Heather Dummitt, Paul Miller, Ronnie Hedden, and David Mullis of Riverwood International (Macon, GA) for providing the mill smelt and raw green liquor samples.

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Fundamentals of Dregs Removal

(Project F01707)

Executive Summary

EXECUTIVE SUMMARY

IPST Goal: Improve dregs separation from green liquor in support of facilitating closed-mill operations

Objective: Determine the effect of elevated levels of non-process elements (NPE's) on the composition and settling rate of green liquor dregs.

SUMMARY:

It is evident that one of the key unit operations in the liquor cycle for controlling NPE build-up is dregs removal. An increase in pulp mill closure or a reduction in the purge rate of green liquor dregs, brought about by a change in physical/chemical properties due to increased closure, will increase the levels of Mg and Mn in the lime cycle and increase the levels of Al, Fe, and Si in both the liquor and lime cycles. Hence, a detailed study of the effect of increased levels of NPE's on dregs removal, and therefore purge of NPE's, was undertaken.

Because actual mill smelt composition may vary from shift to shift, as well as within a given shift, this study worked with a known, representative, synthetic smelt composition (including dregs), and added a fixed amount of specified non-process element chemicals. These were heated to typical smelt bed temperatures and held in a nitrogen atmosphere for a period of time to allow the chemicals to equilibrate. A one-liter stirred batch reactor was designed to carry out these reactions at smelt bed temperatures in the laboratory. All parts which were contacted by molten smelt were fabricated out of alumina to avoid corrosion phenomena and subsequent contamination of the reaction products.

A literature survey of dregs composition, along with analyses of four actual mill dregs samples, identified an "average" dregs composition. Carbon content showed the most variation, with values ranging from under 2% to 35%. This led to an experimental strategy based upon two laboratory smelt compositions featuring low and high carbon content, 2% and 20%. Chemical equilibrium calculations were completed to indicate the compositional changes to be expected when the starting chemicals were subjected to smelting conditions. Within the limitations of the Outokumpu HSC Chemistry for Windows software, the ultimate chemical forms of the NPE's chosen for this study were predicted to be as $Ca(OH)_2$, $Mg(OH)_2$, MnS, SiO_2, $NaAlO_2$, and FeS.

A limited number of successful smelting runs with low carbon content were carried out in the alumina reactor. Replication of experiments was not achieved due to budget and time constraints. The cooled reaction products were then added to hot synthetic weak wash to form a synthetic green liquor. The insolubles represent the dregs for the simulated process. A laboratory settling/permeability apparatus was fabricated to determine dregs settling and filtration properties at normal process temperature; the

insolubles were sampled for chemical analysis. Comparisons were made with the base condition of synthetic smelt vs. that treated at the same conditions with specific levels of NPE's added. To ultimately validate the results, the procedure was repeated starting with an actual kraft smelt and holding it at 850°C for equilibration. After the treated smelt was dissolved in weak wash, the dregs were separated and their properties compared with untreated green liquor dregs obtained from the same mill.

Each NPE addback laboratory run showed an elevated level of the NPE added in the dregs charge for that run. The high Mg runs represent the only case for judging experimental reproducibility in the green liquor dregs formed; agreement was generally within a factor of two.

Starting with mill smelt, NPE concentrations in dregs and the clarified green liquors, heat treated or not, were nearly identical, respectively. The only exception was organic carbon in the dregs where heat treatment resulted in a lower value, probably due to gasification and/or reduction reactions. NPE concentrations in clarified green liquors from mill smelt and from mill green liquor were nearly identical. Dregs from mill green liquor, with and without addition of polymer during clarification, were the same.

NPE concentrations in laboratory green liquors were within a factor of two vs. mill green liquors. Aluminum concentrations in laboratory green liquors are generally higher than in mill green liquors.

Partition coefficients, defined as the ratio of the amount of an NPE in the dregs to that in the corresponding clarified green liquor, were calculated. Results showed that Ca, Fe, Mg, and Mn would be removed effectively by the dregs, even if their concentrations in the liquor cycle increased. Partition coefficients for Na and Si were uniformly low while Al was shown to partition more evenly between dregs and clarified green liquor. Hence, removal of Si and Al from a closed liquor cycle must be by some method other than dregs removal.

After dissolving the smelts in dilute synthetic weak wash, settling rate curves for the dregs showed poor reproducibility within the four conditions where duplicates were run. The Fe and Al addbacks exhibited poor settling characteristics, while Mg and Ca gave the highest settling rates.

Statistical comparison of three addback NPE runs with the base case was made using a method which determines the hypothetical time to reach 10% solids underflow concentration in a continuous green liquor clarifier. Higher clarification times were given by the Fe addback at 98% confidence and Mn at 88%; Ca gave a lower time at the 79% confidence level. Qualitatively, Al also gave a higher settling time. Microscopic particle size analysis showed the Fe addback to have a greater fraction of small particles (<20μm), which would explain a lower settling rate; it also showed Ca to have a greater fraction of large particles (>20μm), resulting in a higher settling rate.

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Filter cake permeability coefficients for the Mn, Mg, and Ca addbacks and heat treated mill smelt were the same as for the base case; Al gave a higher value, while Fe, Si, Mill Smelt (Dissolved), and the Mill Green Liquors were lower. Microscopic analysis of the filter cakes showed the Fe, Si, Mill Smelt (Dissolved), and Mill Green Liquors to have a greater fraction of small particles (<20μm), which should result in decreased permeability coefficients due to relatively high specific surface areas. Permeability coefficients increased at higher vacuum (i.e. higher ΔP), contrary to expectation. Removal of cake fines at higher vacuum resulting in a reduced surface area per unit volume is a plausible explanation.

Mill closed cycle operation must anticipate problems with buildup of Si, Al, and Fe in the liquor cycle due to unfavorable partition coefficients and/or settling rates in the green liquor clarifier.

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1.0 INTRODUCTION

With the enactment of the Cluster Rule, there is a strong push from the environmental sector to close up our pulp and paper mills, minimizing emissions of liquid, solid, and gaseous pollutants, along with usage of fresh water. As moves are made to bring this about, a related problem emerges in the form of non-process elements building up in the liquor streams because opportunities for purge are diminished while input sources remain fixed. Mass balance constraints dictate that concentrations of these unwanted NPE's must increase.

Serious consequences of this build up are felt throughout the pulping liquor recovery cycle of both kraft and soda mills. Unwanted silica and alumina compounds, chlorides, and various metal salts cause operating problems in excessive scale formation on metal surfaces, increased corrosion rates, and reduced effectiveness of the pulping chemicals (1). The latter factor can lower pulp production rate below nameplate capacity, as well as require more energy to produce a pound of product.

Concurrent with the push toward closed-cycle mills is the shift from chlorine based bleaching sequences to non-chlorine based. Examples are oxygen, ozone, and peroxide. For these chemicals to be effective, small amounts of transition metals in the pulping liquors must be avoided (2). Hence, the combination of chlorine-free bleaching with closed-cycle mill operation raises the question of how to purge NPE's to the highest priority level.

At present, the unwanted insoluble materials, called dregs, are continuously purged from the green liquor in the kraft liquor cycle by sedimentation or filtration. The dregs sediments or filter cakes are then landfilled or processed in the mill effluent system. In addition to the NPE's listed above, the dregs contain about 2-30% carbon, giving the material the appearance of a coal slag (3). As kraft pulp mills are forced to effect tighter closure, they can expect the compositional change in their dregs flow to adversely impact their ability to separate and remove the dregs. Dregs physical properties, including density, porosity, and carbon content, will have impact here. In addition, there is concern that trace metals not now detected will rise to levels above present detection limits.

For kraft pulping, the elements Na and S are the principal process elements. The non-process elements include Cl, Al, Si, K, Fe, Ca, Mn, Mg, P, and V. These enter the pulping process with the wood, water, other processing chemicals, and make-up chemicals. They can increase in concentration unless purge mechanisms are provided; presently, these purges are mill solid, liquid, and gaseous effluent streams. Tighter "mill closure" implies a reduction in these effluent discharges in order to decrease both water use and the environmental impact of the pulp manufacturing process.

Although the NPE's tend to be present in low levels, they may have a disproportionate effect on the operation of the mill. Some NPE's (viz. Al, Fe, Mg) are sparingly soluble in green liquor, but more soluble in white liquor. If they are not removed with the dregs, they can carry through to the digester and subsequently cause fouling in the evaporators. Aluminum can trigger evaporator scaling when its

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concentration exceeds 50-100 mg/L in the white liquor. Aluminum can be precipitated from green liquor by the addition of magnesium to form hydrotalcite. Since there is some Mg naturally in the liquor cycle, entering with bleach plant effluent and make-up lime, some Al is being removed by this mechanism in present mill caustic plants.

Magnesium causes problems when it is allowed to accumulate in the lime mud because it calcines in the lime kiln, consuming fuel. The magnesium oxide formed hydrates in the slaker, but it has no causticizing power, making it a heat consuming dead load. Magnesium also causes serious problems in the settling and filtration of lime mud. The finely divided particles of magnesium hydroxide in the dregs cause poor settling rates and a tendency to plug filter cakes. Therefore, it is important to minimize Mg input and control its build-up throughout the caustic plant.

Fe and Mn are other trace elements which can cause problems. The only outlet for these elements is the dregs system. Iron build-up is believed to be a cause of dusting from the lime kiln. The concentration of manganese in the lime cycle is quite low because green liquor clarification is effective in removing Mn.

Some NPE's (viz. Si, P) are soluble in green liquor, but less so in white liquor. Hence, if these are not removed from the green liquor, they can accumulate in the lime mud circuit, lowering lime availability and increasing kiln fuel cost. In the presence of lime, phosphorous is precipitated as apatite, $Ca_5OH(PO_4)_3$. In the lime kiln, apatite converts to calcium phosphate, $Ca_3(PO_4)_2$. Some, but probably not all, of the calcium phosphate converts back to apatite in the causticizing process. P does not precipitate in the green liquor circuit, even when lime is added as a settling or filtration aid. Therefore, its build-up can only be controlled by a purge of lime mud, which is best done at the dregs filter. The recommended bleed is in line with the amount of mud precoat required for optimum operation of the dregs filter.

It is evident that one of the key unit operations in the liquor cycle for controlling NPE build-up is dregs removal. A reduction in the purge rate of green liquor dregs will increase the levels of Mg and Mn in the lime cycle and increase the levels of Al, Fe, and Si in both the liquor and lime cycles. Hence, a detailed study of the effect of increased levels of NPE's on dregs removal, and therefore purge of NPE's, is crucial.

One other NPE that needs to be addressed is chloride. Its removal is difficult because it is soluble and remains with the aqueous liquor streams. Three methods have been practiced commercially in recent years. In the recovery boiler flue gas, SO_2 can react with NaCl, H_2O, and O_2 to form Na_2SO_4 and HCl gas. The HCl can be either scrubbed out of the flue gas by known methods or allowed to escape to the atmosphere (4). An alternative method for chloride removal is to purge NaCl by leaching precipitator dust (5). This method has been developed by Champion International, however it appears cumbersome and expensive. Chloride can also be removed by white liquor evaporation-crystallization. This was practiced as part of the closed mill operation at Thunder Bay, Ontario. It has since been discontinued. A fourth method, being

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developed at IPST, is based upon electrodialysis of a solution of salts from the electrostatic precipitator catch (6).

2.0 EXPERIMENTAL

2.1 Smelt and Green Liquor Formation

A one-liter stirred batch reactor was designed and installed to carry out the smelt formation reactions in the laboratory. All parts which were contacted by molten smelt were fabricated out of alumina (98% pure) to avoid corrosion phenomena and contamination of the reaction products (c.f. Fig. 1).

Chemical analysis of samples of green liquor clarifier underflows obtained from four member company mills, along with available published data on dregs composition (3, 7,8), were used to establish the target baseline starting composition (assuming 95% reduction efficiency) for the study; namely:

Component	Wt.%
Na_2CO_3	74
Na_2S	20
Na_2SO_4	2
NaCl	2
Dregs	2

and the target baseline starting dregs components:

Component	Wt.% A	Wt.% B
$CaCO_3$	65	51
Fe_2O_3	3.5	2.5
$Mg(OH)_2$	12.5	10
MnO_2	6	5.5
SiO_2	10	10
Al_2O_3	1	1
C	2	20
	100	100

The starting dregs compositions listed were changed from what was suggested by the literature. In both cases, the initial SiO_2 was raised by a factor of 10 because partitioning between the green liquor and dregs was found to favor the green liquor by more than what had been reported in the literature. To make up for the increase in SiO_2 charged, the $CaCO_3$ charged was adjusted downward, as this is in great excess to begin with. The carbon content of composition B was lowered to 20% because of a very practical reality - at 35%, the lab smelts could not be removed from the crucibles without breaking them. This seemed very acceptable in light of the 35% number from mill sampling data being somewhat suspect due to poor sampling technique (8-10). A recent study sampled many kraft mills and reported elemental analyses for the dregs (separated

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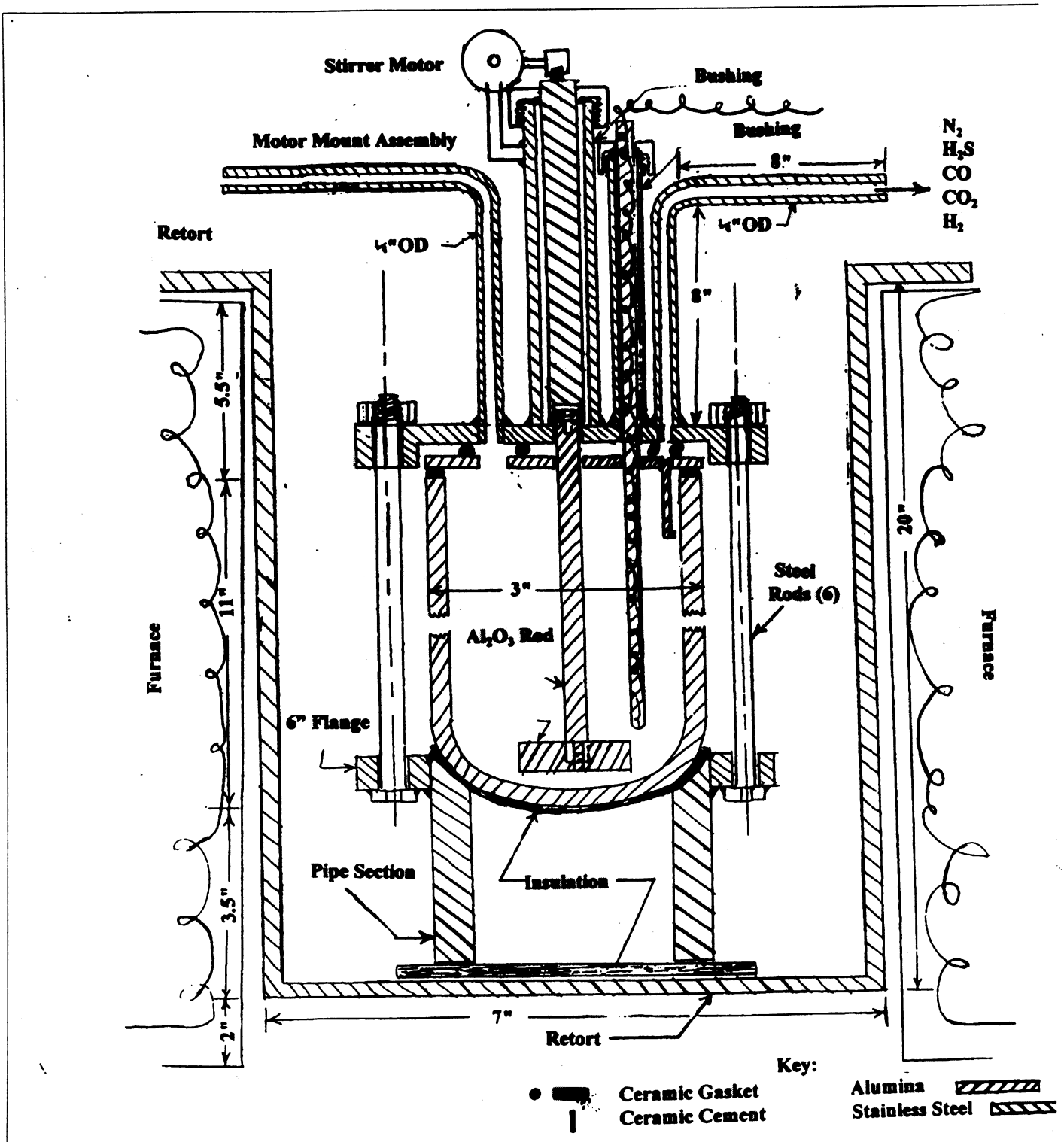

Fig.1 - Laboratory Smelt Reactor

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from green liquor samples) ranging from 0.6 to 5.7%, dry basis (11). Hence, composition A appears to be the more representative value.

The synthetic smelt chemicals (including dregs), along with the specified non-process element chemicals, were added to the alumina reactor. These were then heated to 850°C (typical recovery boiler smelt bed temperature) and held in a nitrogen atmosphere and stirred for one hour to allow the chemicals to equilibrate under non-oxidizing conditions. At the end of the run as the heat was turned off, the stirrer and thermowell were removed from the smelt to prevent them from being trapped during solidification. The cooled reaction products were then removed (with difficulty) from the reactor, ground in a nitrogen-purged glove bag to prevent air oxidation of sulfide, and then added to a hot synthetic weak wash (2.5% NaOH) to form a synthetic green liquor.

As the actual experimental sequence unfolded, equipment and operating problems severely slowed the project down. The solidified smelt did not always contract away from the alumina wall, making removal from the reactor labor intensive. Attempts to "mine" this smelt often led to a cracked alumina vessel, with concomitant contamination of the smelt product. Several runs were terminated early because of a broken agitator shaft or thermowell, both of which were fabricated out of alumina.

Initial attempts to run with the high carbon content dregs met with consistent failure because of the tenacity of the cooled product smelt cemented to the alumina wall. Trial and error with successive reduction of the amount of carbon charged showed that a maximum of 20% was the workable limit. For practical reasons, it was decided to complete the 2% carbon in dregs runs before going to the higher concentration of carbon. As the program unfolded, the experiments with the higher carbon dregs composition were never completed due to budgetary constraints and lack of time.

Settling and filtration rates of the insolubles were determined at 80°C; these were then filtered out and washed with hot water. These washed insolubles represent the dregs for the simulated process and were sampled for chemical and physical property analyses. The physical properties of interest are density, porosity, and particle size distribution. Comparisons were then made with the base condition of synthetic smelt treated at the same conditions with no NPE's added.

Smelt and green liquor samples were obtained from a Georgia kraft mill to provide validation of the laboratory procedures. Green liquors were produced from the mill smelt sample by dissolution in weak wash per the normal laboratory procedure. One-half of the as-received mill smelt was dissolved without further processing, while the other half was subjected to the normal laboratory "smelting" procedure before dissolving. Producing green liquors from both these paths enabled validation of the high temperature treatment step as a way to produce dregs in the laboratory with representative physical properties.

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2.2 Dregs Separation

Because dregs removal technology is no longer limited to clarification, with the advent of developing crossflow filtration, separability of dregs from green liquor must be characterized for both sedimentation and filtration. A laboratory apparatus and procedure reported for lime mud separation was used to determine the settling characteristics of the dregs produced in the lab runs and suspended in 80°C synthetic weak wash, as well as those in the mill green liquor (12). Also determined was the permeability of the resultant filter cakes (c.f. Fig. 2) at 80°C.

The sedimentation column consisted of a graduated plexiglas tube (5 cm. ID, 50 cm. height) enclosed in a 30 cm. O.D. transparent air bath controlled slightly above 80°C. Preheated raw green liquor (850 mL) was added to the settling column following the addition of 3 ppm polymer (Betz/Dearborn Perform PA8990®). The filter base supporting a 0.45 μm polyether sulphone filter was connected to a vacuum flask outside the air bath. A constant vacuum was maintained by manually setting an air bleed rate into the line ahead of the vacuum pump. A maximum vacuum of about 30 kPa was limited by the vapor pressure of water at process temperature (viz., 48 kPa at 80°C). Initial column height was recorded; then the rate of descent of the mud-liquor interface was observed with time.

The apparatus was initially tested without difficulty using fine $CaCO_3$ particles in H_2O. Subsequent tests with green liquor and dregs showed that the settling rate determinations were not going to be easy. Locating the interface of the settling dregs with the naked eye was complicated by the nearly opaque appearance of the green liquor. A 3 amp laser was procured to assist with this activity. By shining the laser downward through the liquor in the column, the depth of penetration of the light beam identifies the "interface" between the settling solids and the supernatant liquid. The laser can also be used to locate at what height the cake is building. By shining the laser through the side of the column and slowly moving downward, the light penetrates about the same distance radially until the surface of the cake is encountered, at which point there is zero penetration.

The reciprocal of the resistance to flow of a liquid through a bed of packed particles is characterized by a parameter called permeability (13). It depends upon the actual structure of the bed, including the specific surface area of the particles, the void fraction, and the tortuosity, radius, and surface roughness of the pores in the particles. To prepare the bed for permeability measurements, green liquor was allowed to flow by gravity through the settled solids. The frictional drag of the flowing liquid compacted the cake particles. A constant liquid head was maintained during the compaction stage by feeding hot weak wash to the column to replace the liquid exiting the cake. When the thickness of the compacted cake was constant, the flows were shut off and the cake thickness and height of liquor in the column measured. From the liquor height in the column, the fluid pressure under which the cake was compressed could be calculated. Because cake thickness was generally less than 1 cm and grew very slowly with time, a cathetometer had to be installed to accurately measure this variable.

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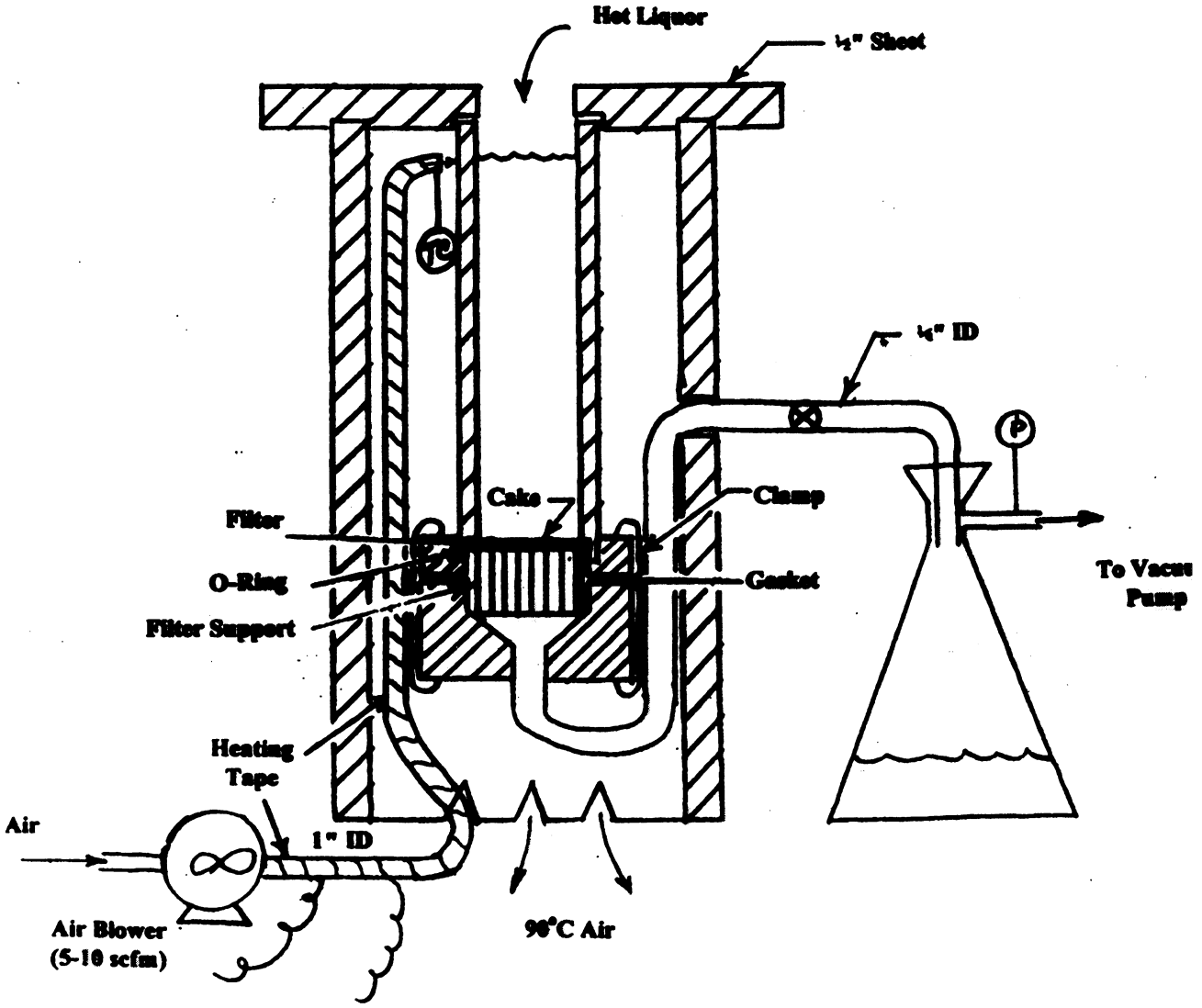

Fig. 2 - Sedimentation/Permeability Apparatus

Cake permeability was determined by the pressure-decline permeability method, which yields bed permeability compressed at a fixed fluid pressure (12). This was done by opening the stopcock in the outflow line and measuring the liquid meniscus as a function of time, using the graduated scale on the side of the column. These measurements yield the permeability of the cake compressed at a fixed fluid pressure. Two levels of compression were obtained by varying the vacuum on the system (5" and 8.5" Hg) while maintaining a constant level of fluid in the column.

The bed permeability, K, is calculated from Darcy's Law, knowing the volumetric flow rate, Q, through a cake of thickness L and cross-sectional area A:

$$Q = \frac{KA\Delta P}{\mu_f L}$$

where ΔP is the fluid pressure drop across the bed and μ_f is the viscosity of the fluid (measured to be 0.7 cP).

As the dregs settled, the clarified green liquor exhibited noticeable convection currents, as evidenced by small dregs particles moving upward in some zones and downward in others. This was attributed to the settling solids displacing liquid which can't flow through the filter cake fast enough to maintain a uniform downflow. To make sure that thermal convection currents were not the cause, the temperature profile of the liquor in the heated column was checked axially and found to be uniform. Although the settling rate of the dregs was very slow and took hours, when left to run overnight, the dregs did settle out completely, leaving a clear green liquor.

2.3 Analyses

Clarified green liquor (CGL) was analyzed for carbonate, hydroxide, sulfate, sulfite, thiosulfate, and chloride concentrations using Capillary Ion Electrophoresis (CIE). In addition, carbonate, hydroxide, and sulfide concentrations were determined by the ABC titration method. Smelt, green liquor, and dregs samples were analyzed for trace metals using a nitric acid, hydrogen peroxide, and hydrochloric acid digestion procedure, followed by analysis by Inductively Coupled Plasma Emission Spectroscopy (ICP). Silicon analysis for the solid smelt and dregs samples required preparation by a caustic fusion procedure developed at IPST.

Dregs samples proved to be very difficult to analyze. Nitric acid microwave digestion prior to acidification was performed as standard sample preparation; a caustic fusion procedure was used for samples with appreciable silicon levels [IPST Standard Operating Procedure 35_PM_1005]. Dregs samples were also sent out to Huffman Labs for determination of Total Organic Carbon (TOC).

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3.0 Smelt Composition Modeling

Theoretical chemical equilibrium calculations were undertaken using Outokumpu HSC Chemistry for Windows (by license) for comparison with the experimental results. This software package computes chemical reaction equilibria for specified input chemicals and temperature using an extensive thermochemical database and minimization of Gibbs free energy. A serious limitation to the results generated is in the number of compounds considered. The user must specify which compounds are to be considered and only those will be in the calculation. One serious omission is Pirssonite ($Na_2Ca(CO_3)_2$) which is known to be present in scale deposits in green liquor processing equipment. Nonetheless, the calculations should reflect what forms the majority of the input chemicals should ultimately assume. Chemical species showing less than 2 ppm in the total smelt were arbitrarily ruled to not be present. Results are shown in Appendix C. These are summarized below:

Input Chemical	Change in Smelted Chemicals
Na_2CO_3	0.3-1.3% Gain (except for high Mg)
Na_2S	2-5% Decrease
NaCl	No Change
NaOH	Formed
$CaCO_3$	10-30% Decrease
Fe_2O_3	FeS, FeS_2, FeO Formed
$Mg(OH)_2$	MgO, $MgCO_3$ Formed
MnO_2	MnS, MnO Formed
SiO_2	No Change
Al_2O_3	$NaAlO_2$ Formed
C	30-100% Decrease (except for high Mg)
S	Formed (except for high Mn)

It is interesting to note in the high Mg case, Na_2CO_3 is predicted to be decreased and carbon formed, somehow. In the high Al case, not all of the Al_2O_3 would be converted to the aluminate. In the high Mn case, no FeS_2, $MgCO_3$, or sulfur would be formed.

4.0 RESULTS

4.1 Smelt Formation

Table 1 summarizes the runs carried out successfully in the laboratory smelter using commercially available reagent chemicals; also run in the series was Run 093, which was kraft smelt from a Georgia mill. Actual weights of chemicals are summarized in Appendix A.

Table 1. Initial Composition of Laboratory Smelts (Wt.%, Dry Basis)

Species	Run 040 Base	Run 045 Fe x 10	Run 049 Mg x 10	Run 053 Mn x 10	Run 057 Al x 10	Run 083 Si x 5	Run 090 Ca x 10	Run 092 Mg x 10
Na2CO3	70.6	70.14	69	69.8	70.5	70.04	62.17	69
Na2S	23.5	23.35	22.9	23.3	23.5	23.31	20.51	22.9
Na2SO4	1.95	1.94	1.91	1.93	1.95	1.93	1.72	1.91
NaCl	1.95	1.94	1.91	1.93	1.95	1.92	1.72	1.91
CaCO3	1.3	1.3	1.3	1.3	1.3	1.3	13	1.3
Fe2O3	0.07	0.7	0.07	0.07	0.07	0.07	0.07	0.07
Mg(OH)2	0.25	0.25	2.5	0.25	0.25	0.25	0.25	2.5
MnO2	0.12	0.12	0.12	1.2	0.12	0.12	0.12	0.12
SiO2	0.2	0.2	0.2	0.2	0.2	1	0.2	0.2
Al2O3	0.02	0.02	0.02	0.02	0.2	0.02	0.02	0.02
C	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04

Overall mass balances for the laboratory smelt formation runs are shown in Table 2. The product smelts all showed significant weight loss, generally 17-21%, except for the run starting with mill smelt. This is attributed to the loss of water of crystallization originating from the Na_2S crystals charged (c.f., Appendix A); this claim is supported by the mill smelt case where no water of crystallization would be expected. There was, however, a small loss of organic carbon in the mill smelt case (c.f. Table 4).

Table 2. Overall Mass Balances for Laboratory Smelts (g.)

	Run 040 Base	Run 045 Fe x 10	Run 049 Mg x 10	Run 053 Mn x 10	Run 057 Al x 10	Run 083 Si x 5	Run 090 Ca x 10	Run 092 Mg x 10	Run 093 Mill,smlt
Chems In	500.0	500.0	499.9	499.9	500.0	500.0	499.9	500.3	410
Xtln.H_2O	244.0	242.5	238.4	241.4	243.6	242.1	214.9	238.7	n.a.
Total In	744.0	742.5	738.3	741.3	743.6	742.1	714.8	739.0	410
Product	604.4	588.4	596.1	608.7	603.5	616.2	589.0	608.0	406
Unacctd.	135.6	154,1	142.2	132.6	140.1	125.9	125.8	131.0	4
%Closure	81.2	79.2	80.7	82.1	81.2	83.0	82.4	82.3	99.0

4.2 Green Liquor Formation

The smelts produced in the laboratory were dissolved in a synthetic weak wash (2.5% NaOH) at 80°C. The dregs were settled out and removed for analysis. Tables 3 and 4 summarize the NPE concentrations in the clarified product green liquors and the separated dregs; included are the green liquors made from the mill smelt sample, both with and without smelting in the laboratory reactor, along with an actual mill green liquor sample. Because of time and budget limitations, the only duplicate runs completed were with high Mg (Runs 049 and 092).

Table 3. NPE's in Clarified Green Liquor (mg/kg)

Metal	040 Base	045 Fe x 10	049 Mg x 10	053 Mn x 10	Run 057 Al x 10	Number 083 Si x 5	and 090 Ca x 10	Type 092 Mg x 10	093 Mill, smltd	095 Mill, dssIvd	100 Mill GL
Ca	10.6	10.8	12.5	9.80	9.65	16.6	19.2	19.8	18.3	16.5	16.7
Fe	0.37	0.13	0.12	0.40	[redacted]	0.80	0.82	0.93	0.91	0.61	0.63
Mg	2.12	2.70	2.45	1.76	1.85	2.18	2.07	2.83	1.49	1.79	1.92
Mn	0.09	0.11	0.08	0.12	0.13	0.12	0.14	0.34	0.14	0.15	0.06
Si	145	258	128	416	194	469	[redacted]	413	200	242	174
Al	37.4	18.5	[redacted]	24.0	[redacted]	13.5	27.5	17.0	12.8	12.2	7.9

The clarified green liquors showed a number of interesting characteristics:

- NPE concentrations in the clarified green liquors made from mill smelt were nearly identical, whether the smelt was thermally treated or not; they were also nearly identical to the mill green liquor.
- NPE concentrations in the laboratory clarified green liquors were generally within a factor of two when compared with the mill green liquors. Al concentrations were consistently high relative to the mill liquors (Run 049 appeared to have a suspiciously low value and needs to be duplicated).
- The addback runs showed no unusual behavior except for Run 057 where a high Al input resulted in high Al in the green liquor. The high Fe value shown in this run was highly suspicious, and therefore this run would need to be duplicated before any conclusions could be made.

Table 4. NPE's in Dregs Produced (wt.%, dry basis)

Elmnt	Run 040 Base	Run 045 Fe x 10	Run 049 Mg x 10	Run 053 Mn x 10	Run 057 Al x 10	Run 083 Si x 5	Run 090 Ca x 10	Run 092 Mg x 10	Run 093 Mill, smltd	Run 095 Mill, dssIvd	Run 100 Mill GL + Polymer	Run 200 Mill GL as rec'd
Ca	12.50	5.59	10.65	9.86	19.00	18.50	[redacted]	7.68	12.20	12.00	6.40	6.01
Fe	1.49	14.25	1.23	1.51	3.02	3.18	[redacted]	1.31	5.25	3.98	2.99	3.54
Mg	2.73	2.43	19.25	2.63	5.79	4.79	[redacted]	[redacted]	8.11	7.19	8.35	10.10
Mn	2.24	2.21	1.75	[redacted]	4.17	4.00	[redacted]	1.68	3.42	3.24	3.87	4.54
Si	0.30	0.12	0.32	0.07	0.13	[redacted]	0.08	0.10	0.12	0.35	0.36	0.27
Al	0.46	0.34	0.44	0.39	[redacted]	0.62	[redacted]	1.07	1.40	1.50	1.91	2.33
Org.C	n.a.	n.a.	n.a.	<0.05	0.38	0.74	0.08	0.15	[redacted]	[redacted]	1.27-	1.37

The dregs data in Table 4 also show some interesting concentration effects:

- NPE concentrations in dregs resulting from mill smelt are nearly identical, whether or not the smelt was heated in the lab reactor; the only exception being organic carbon. The deficiency in organic carbon brought about by the laboratory smelting procedure is most likely due to a combination of gasification and sulfate reduction. The high organic carbon value for the dregs resulting from dissolution of solid mill smelt in the laboratory (Run 095) relative to mill green liquors (where molten smelt is dissolved) is consistent with this in that there could have been some carbon gasification in the molten mill smelt as it contacted water in the dissolving tank.

- The high Mg runs (049, 092) represent the only case of gauging reproducibility in the green liquors formed. Agreement is fair.

- Dregs from the mill green liquor, with or without addition of polymer during clarification, are essentially identical.

- Each NPE addback laboratory run shows an elevated level of the respective NPE in the dregs for that run. It should be noted with the high Ca run (090), that concentrations of the other NPE's are all significantly lower than the other runs where standard concentrations of the respective NPE's were charged. This is a result of having so much calcium present at the start.

At this point it is important to compare the laboratory results in Table 4 with the available mill dregs compositions reported in the literature and elsewhere. These data are summarized in Table 4M; the first five are from Swedish mills, the next four from Canadian mills, the next four from southeastern U.S., and the last from Wisconsin.

Table 4M. NPE's in Mill Dregs (Wt.%, dry basis)

						Mill Designation									
Elemnt (Ref.)	A (3)	B (3)	C (3)	D (3)	E (3)	ACA (8)	BCA (8)	CCA (8)	DCA (8)	GP (7)	GA (7)	PA (7)	VA (7)	WI (7)	Avg.	St.Dv.
Si	0.2	0.4	0.01	0.2	0.3	0.12	0.3	1.47	0.33	0.46	0.54			1.01	0.45	0.41
Al	0.7	0.5	0.9	0.02	0.9	0.29	0.43	0.11	0.17	0.19	0.33	0.23	1.23	0.4	0.46	0.35
Ca	24.2	28.9	27.1	16.5	7.8	26.92	42.3	4.57	2.38	7.19	17.87	19.35	14.21	18.87	18.44	11.00
Fe	0.8	1.2	1	1.5	1.9	0.9	1.57	0.31	0.31	0.62	0.68	0.7	1.05	0.62	0.94	0.47
Mg	1.9	2.8	4.5	2.2	3.7	2.54	5.64	3.68	0.9	1.67	2.21	1.68	4.06	2.62	2.86	1.30
Mn	0.9	2.3	2.1	2.7	1.9	1.73	1.57	0.08	0.33	0.35	1.92	1.35	3.17	1.06	1.53	0.92
K						0.64	0.1	5.18	1.96	1.07	0.14		0.16	1.08	1.29	1.70
Na	6.3	1.8	0.6	12.1	9.9	8.41	1.69	25	3.22	19.07	3.93	12.28	3.11	10.48	8.42	7.09
S	1.3	2.4	3.1	1.2	4.2	0.12	0.3	1.47	0.33	4.6	2.54	1.39	3.29	2.28	2.04	1.41
P	0.2	0.4	0.2		0.03						<.01	0.01	0.01	0.01	0.12	0.15
Cl	0.01	0.03	0.06		0.01					0.32				0.22	0.11	0.13
O(CO3)	32.8	33.6	31.6	29.6	16.2					23.84	24	38.6	18.8	32.8	28.18	7.17
C(CO3)	8.2	8.4	7.9	7.4	4					5.96	6	9.4	4.7	8.2	7.02	1.76
C(Org.)	9.3	2.1	2.1	1.5	20.4	3.32	1.79	0.58	5.68	15.35	33.2	2	31.9	2.8	9.43	11.38
H,O(diff)	13.2	15.17	18.83	25.08	28.76					19.31	6.64	13.01	14.31	17.55	17.19	6.33
TOTAL	100	100	100	100	100					100	100	100	100	100		

The mill literature data show considerable variation, which could be expected from such different geographical locations at different time periods and with different (and sometimes unknown) sampling techniques and analytical methods. The last two columns tabulate the averages and standard deviations for each of the NPE's listed. Comparison of Table 4 with Table 4M shows fair agreement with some notable exceptions:

- The Fe and Mn concentrations for the Al and Si addbacks and mill derived dregs are more than 2σ above the literature averages for Fe and Mn.
- The Mg content for the Al addback and each mill derived dregs is more than 2σ above the literature average for Mg.
- The Al concentrations for the mill derived dregs are more than 2σ above the literature average for Al.
- The Si concentrations for all addbacks (except for the Si case) and mill derived dregs are within 1σ of the literature average for Si.
- Organic carbon levels for all addback runs and mill derived dregs are all below the literature average (which has a large standard deviation).
- The Ca concentrations for all addbacks are within 1σ (except for the Ca and Fe addbacks) of the literature average; Ca in lab dregs from mill smelt are less than 1σ below the literature average, while Ca in dregs from mill green liquor are between 1 and 2σ below the literature average.

An important quantity of interest is how the NPE's in the product smelt partition themselves between the clarified green liquor and the dregs fraction. Partition coefficients (K_{DG}), defined as the ratio of the amount of metal element in the dregs fraction to the corresponding metal amount in the clarified green liquor, were determined, based upon the metals analysis and the total mass of green liquor solids and dregs. Results are summarized below in Table 5; included in parentheses is the mass closure (Out/In) data for each metal. As was expected, K_{DG} for Na was always less than 0.01.

Table 5. Partition Coefficients (M in Dregs/M in GL)

Partition Coefficient (Mass Out/Mass In)

Run	Addback	Ca	Fe	Mg	Mn	Si	Al
040	Base	37.3 (0.56)	130 (0.70)	40.3 (0.60)	741 (0.66)	0.07 (1.18)	0.42 (3.52)
049	Mg × 10	31.2 (0.58)	355 (0.67)	275 (0.51)	834 (0.65)	0.10 (1.06)	13.1 (1.21)
053	Mn × 10	40.7 (0.57)	150 (0.89)	59.8 (0.74)	7139 (0.80)	0.01 (3.22)	0.67 (2.70)
057	Al × 10	42.5 (0.60)	18.1 (1.05)	67.7 (0.90)	687 (0.89)	0.01 (1.55)	0.34 (0.78)
083	Si × 5	37.7 (0.91)	135 (1.62)	74.5 (1.16)	1178 (1.3)	0.01 (0.74)	3.26 (3.86)
090	Ca × 10	279 (0.72)	78.1 (0.93)	57.9 (0.81)	642 (0.79)	0.02 (4.06)	0.40 (2.20)
092	Mg × 10	23.0 (0.67)	82.7 (1.16)	462 (0.91)	294 (0.95)	0.01 (3.26)	3.83 (5.68)
093	Mill, smltd	2.6	8.7	90.2	71.8	0	0.52
095	Mill, dsslvd	4.4	39.7	24.4	131	0.01	0.75
100	Mill GL	2	25	22.6	354	0.01	1.24

Important observations from Table 5 include:

- NPE partition coefficients for mill green liquor (Run 100) and green liquor made from solidified mill smelt (Run 095) are essentially the same. Green liquor from heat treated mill smelt (Run 093) shows a high K_{DG} value for Mg and low values for Fe and Mn, relative to green liquor from solidified smelt or from mill green liquor.

- Ca partition coefficients for the addback runs are generally an order of magnitude higher than for the mill samples, most likely because of the high Ca levels used in the starting chemicals for the addback runs. The singularly high K_{DG} value for the Ca addback run (090) shows that calcium will be removed effectively by the dregs, even if Ca concentrations in the liquor cycle increase.

- Fe, Mg and Mn partition coefficients for the addback runs are higher than for the mill samples. The singularly high K_{DG} values for the Mg and Mn addback runs (049, 092, 053) show these metals will be removed effectively by the dregs, even if their concentrations in the liquor cycle increase.

- Partition coefficients for Si are low in all cases, implying that removal from the liquor cycle must be by some method other than dregs removal.

- Al partitions fairly evenly between the dregs and CGL, even with the Al addback case. Hence, high Al input to the liquor cycle will not be controlled by dregs removal.

Overall solids mass balances for the green liquor formation step are summarized in Table 6. Generally, balances were within ± 3% of full closure, with the exception of the Ca and Mg addback runs. Individual NPE mass balance closures (in parentheses in Table 5) were variable, with Si showing a significant gain in all runs but the high-silicon run. There are two analytical procedures for Si, with both having uncertainties. The results shown are based on using a caustic digestion procedure where some contamination is suspected. The alternative acid digestion procedure gave lower Si values, but there is a question of all the sample being solubilized in this method.

Mass balance closures for aluminum were also high, except for the run with high aluminum. Rather than analytical problems, the cause for this is most likely some erosion/corrosion of the alumina smelter, which compositionally was about 98% Al_2O_3.

Table 6. Overall Mass Balances for Laboratory Green Liquor Solids

	Run 040 Base	Run 049 Mg x 10	Run 053 Mn x 10	Run 057 Al x 10	Run 083 Si x 5	Run 090 Ca x 10	Run 092 Mg x 10	Run 093 Mill,smlt	Run 095 Mill,dsslvd
Smelt In	597	596.1	603	603.5	612.5	589	608	406	410
Wk Wsh NaOH	74.6	74.5	75.4	78.1	76.6	73.6	76.0	50.8	51.3
Total Solids In	671.6	670.6	678.4	681.6	689.1	662.6	684.0	456.8	461.3
GL Solids	641.6	673.3	668.8	683.8	683.2	653.7	784.4	466.4	468.3
Dregs	11.3	13.7	14.5	8.0	12.4	47.5	21.5	1.5	1.5
Total Slds Out	652.9	687.0	683.3	691.8	695.6	701.2	805.9	467.9	469.8
%Closure	97.2	102.5	100.7	101.5	100.9	105.8	117.8	102.4	101.9

The partition coefficient results in Table 5 were used to calculate the per cent of each input NPE that was found in the clarified green liquor (on a normalized basis). Summarized in Table 7, this is a more traditional way of viewing the distribution of NPE's between dregs and clarified green liquor.

Table 7. Wt.% of Input NPE in Clarified Green Liquor

Run	Addback	Ca	Fe	Mg	Mn	Si	Al
040	Base	2.6	0.8	2.4	0.13	93.9	70.3
049	Mg x 10	3.1	0.3	0.4	0.12	91.2	7.1
053	Mn x 10	2.4	0.7	1.7	0.01	99.0	59.9
057	Al x 10	2.3	5.2	1.5	0.15	98.9	74.8
083	Si x 5	2.6	0.7	1.3	0.08	99.1	23.5
090	Ca x 10	0.4	1.3	1.7	0.16	98.1	71.6
092	Mg x 10	4.2	1.2	0.2	0.34	98.6	20.7
093	Mill, smltd	28.1	10.3	1.1	1.37	99.7	65.7
095	Mill, dsslvd	18.5	2.5	3.9	0.76	99.1	57.3
100	Mill GL	33.4	3.8	4.2	0.28	98.9	44.6

These results confirm that:

- Si stays predominantly with the clarified green liquor (CGL) while Al is distributed nearly evenly between the CGL and the dregs.

- Ca, Fe, Mg, and Mn stay predominantly with the dregs. Ca in the mill samples shows higher values in CGL than the laboratory Ca, again, because of the high Ca input in the lab runs (almost all of which is insoluble).

- All NPE's in mill smelt that was cooled and dissolved in synthetic weak wash (Run 095) are distributed essentially the same as mill green liquor (Run 100). This implies that allowing smelt to freeze before being dissolved gives results similar to mill smelt dissolved straight from a molten state, thus validating the second half of the laboratory procedure.

- Validation of the laboratory smelting procedure is confirmed by comparing Runs 093 and 095 in Table 7. Ca, Al, Si, and Mn show consistency within a factor of two; the lab smelting procedure leaves Fe in a more soluble (4x) and Mg in a less soluble (×¼) form when compared to mill smelt just dissolved without additional "smelting".

These same data in Table 7 can be expressed in terms of % removal from the raw green liquor and are presented in Table 8. Also included in the table are some mill data that were recently published for four Canadian mills (11).

Data reproducibility can only be seen in the high Mg case, namely Runs 049 and 092. The agreement in % Removal of NPE's from Green Liquor is very good for Ca, Fe, Mg, and Mn; Al and Si show greater variation. Interestingly, the Al and Si data reported for the Canadian mills also show significant variation. The negative values in Table 8 are a result of poor mass balances.

Table 8. Comparison of Laboratory and Mill Clarified Green Liquors

% Removal from Green Liquor

Run	Addback	Ca	Fe	Mg	Mn	Si	Al
040	Base	97.4	99.2	97.6	99.9	6.1	29.7
[redacted]							
053	Mn x 10	97.6	99.3	98.3	99.9	1.0	40.1
057	Al x 10	97.7	94.8	98.5	99.8	1.1	25.2
083	Si x 5	97.4	99.3	98.7	99.9	0.9	76.5
090	Ca x 10	99.6	98.7	98.3	99.8	1.9	28.4
[redacted]							
093	Mill, smltd	71.9	89.7	98.9	98.6	0.3	34.3
095	Mill, dsslvd	81.5	97.5	96.1	99.2	0.9	42.7
100	Mill GL	66.6	96.2	95.8	99.7	1.1	55.4
ACA	(16)	66.2	50.0	79.2	65.9	16.9	(-5.5)
BCA	(16)	93.6	88.7	94.2	91.4	0.0	62.2
CCA	(16)	98.5	61.6	95.8	85.4	33.5	66.7
DCA	(16)	71.9	83.7	62.0	59.0	(-5.1)	34.2

Mean values in NPE removal for three groupings - the laboratory addback runs (040-092), the laboratory mill derived liquors (093-100), and the Canadian mill liquors – were computed and the t-test applied to identify any significant differences. Comparison of the mill derived vs. Canadian mill liquors showed the mill derived liquors to have better removal of Fe, Mg, and Mn, poorer removal of Si, and the same degree of removal for Ca and Al. Comparison of the laboratory addbacks vs. Canadian mill liquors showed the same effects, only stronger.

4.3 Dregs Settling Rates

Dregs settling rates in 80°C green liquor were determined by recording the height of the line of demarcation between the settling solids and the clear supernatant liquor. Typically, there are three zones of settling: an initial constant rate zone where particles are considered non-touching; an intermediate zone where settling rate drops progressively

as regions of higher solids concentration, but lower flux, start to propagate upwards from the bottom of the column; and a final zone where the settling solids reach a concentration where the solids contact each other to form a structure that develops compressive strength (14). In this third zone, most of the weight of the solids is supported hydrodynamically, however a fraction of this weight is available to produce solids stress and force the trapped fluid to move upward through the compacted bed until the final sediment structure carries the entire weight of the particles and no further compression occurs. In simple terms, the three zones can be referred to as free settling, hindered settling, and compression settling.

Because of the strong concentration dependence of settling rate, each settling curve determination was started with the same initial concentration of smelt in green liquor, resulting in nearly equal concentrations of undissolved dregs particles. In this way, differences in the settling curves can be ascribed to variations in the size, shape, and density of the aggregate particles.

The various settling curves obtained for laboratory smelts, including the base case and NPE addbacks, and mill derived smelt and green liquor, are shown in Figs. 3-11. The difficulty in obtaining reproducible data is underscored by four of the runs (040, 045, 053, 090), with the Ca and Mn addbacks looking the best. The base case (Fig.4) was run when there were still problems with some green liquor bypassing the filter paper due to an imperfect seal. Fig.3 shows a composite of all the laboratory green liquors, with the Fe and Al runs qualitatively exhibiting poor settling characteristics and Mg and Ca the best. Fig.11 shows the settling curves for green liquor derived from mill smelt, both *as is* and put through the laboratory smelting procedure; it also shows settling curves for raw green liquor obtained from the same mill, without and with polymer added in the lab. Those curves look similar, except for the mill smelt that was thermally treated (093); it settled at a lower rate.

The problem at this point is how to use the three different settling rates contained in each of the settling curves for quantitative comparison purposes. A method developed by Talmadge and Fitch (15) takes the batch settling data and graphically determines the time to reach a desired underflow concentration in a continuous clarifier. This method allows a semi-quantitative assessment of settling efficiency without having to determine the two breakpoints in the settling curves, which is difficult at best. The method is somewhat subjective in that tangents to the settling curve for the initial, intermediate, and final settling zones must be established. Results are shown below in Table 9, using a design target underflow solids concentration of 10%, which is typical for a green liquor clarifier.

There are limited data to make statistical comparisons with the base case. Duplicates were run for four cases, showing varying degrees of precision. Comparison of the addbacks (Runs 045, 053, and 090) with the base case (Run 040), by employing the statistical t-test for significant differences between means, shows that high Fe gives a higher clarification time at the 98% confidence level. Similarly, the clarification time

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Fig. 3 - Settling Rate (NPE Addbacks)

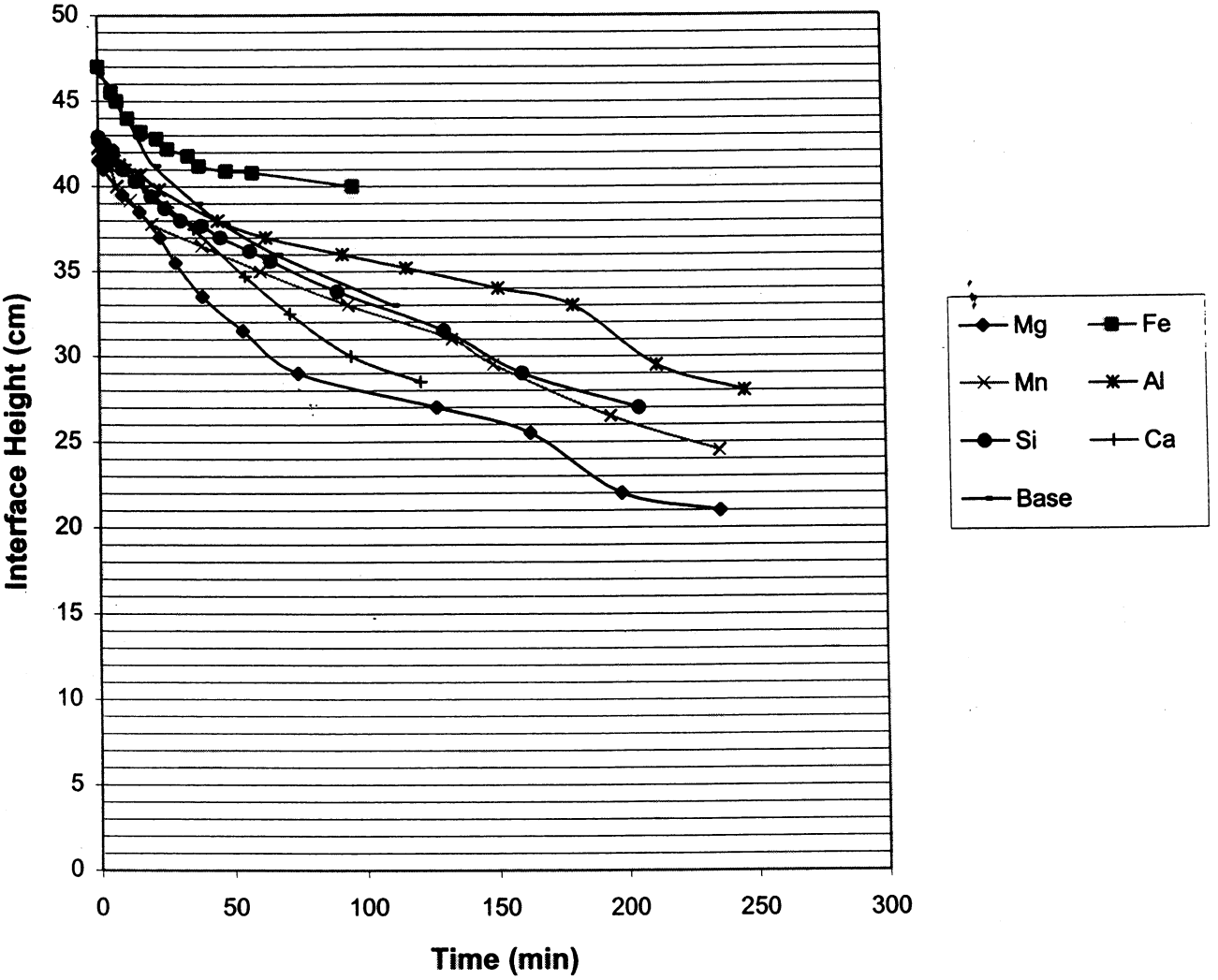

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Fig. 4 - Settling Rate (Base Case)

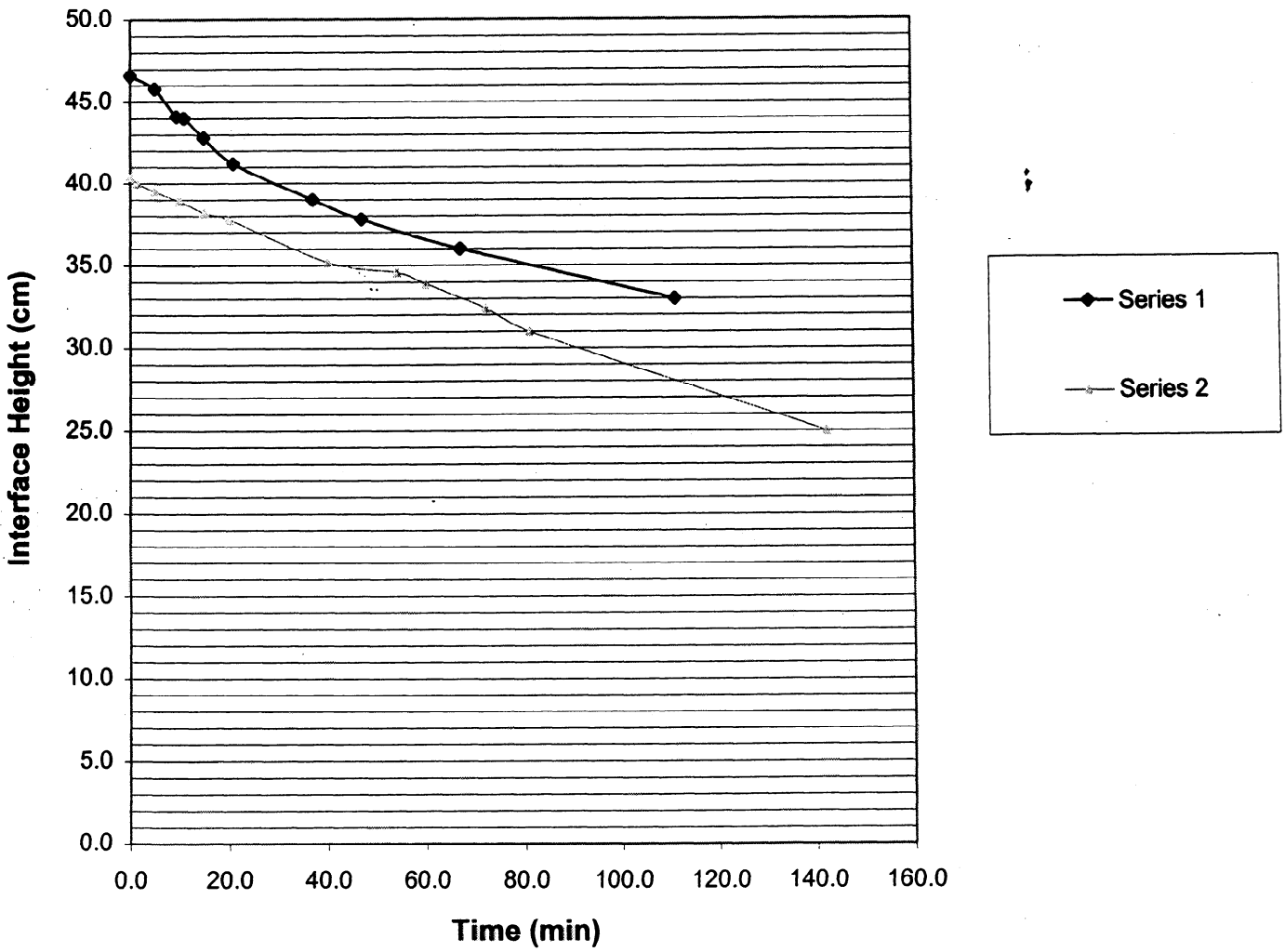

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Fig. 5 - Settling Rate (10XFe)

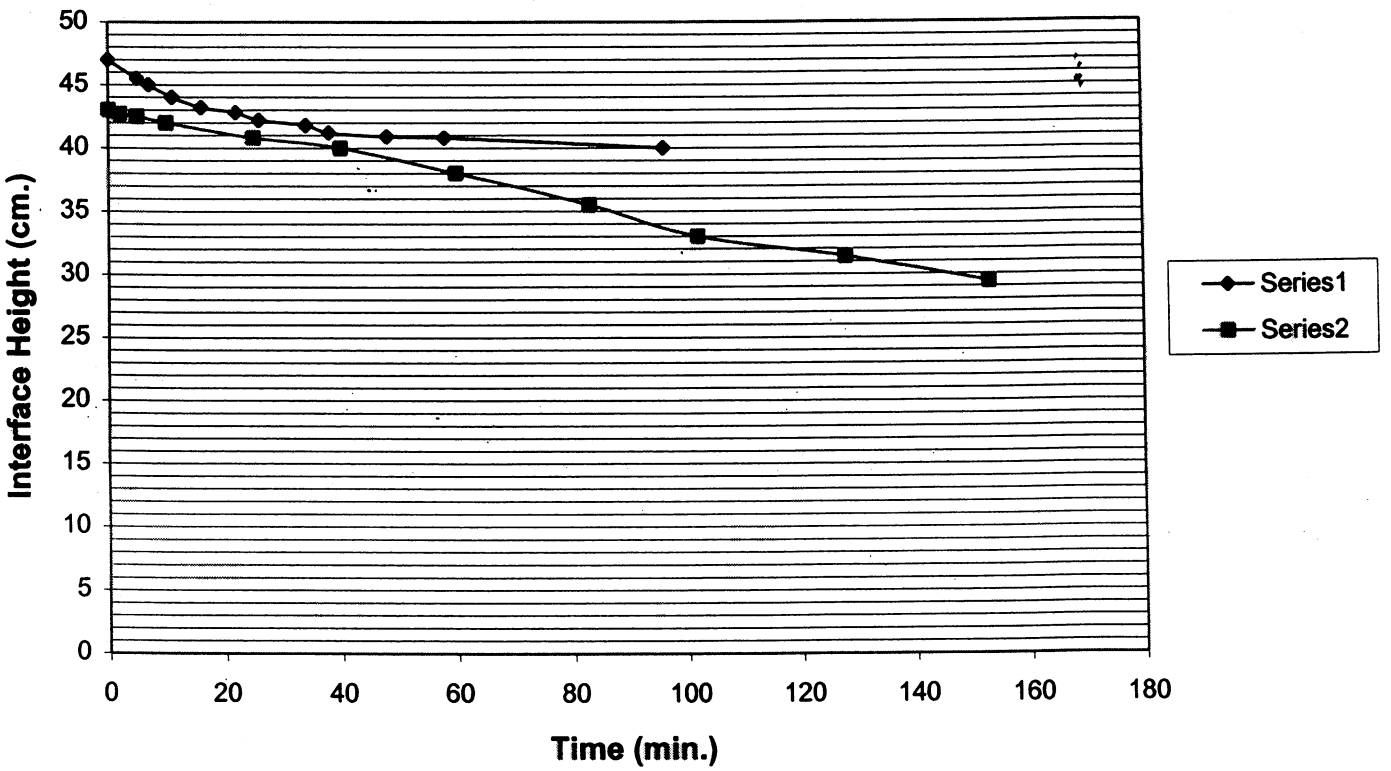

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Fig. 6 - Settling Rate (10XMg)

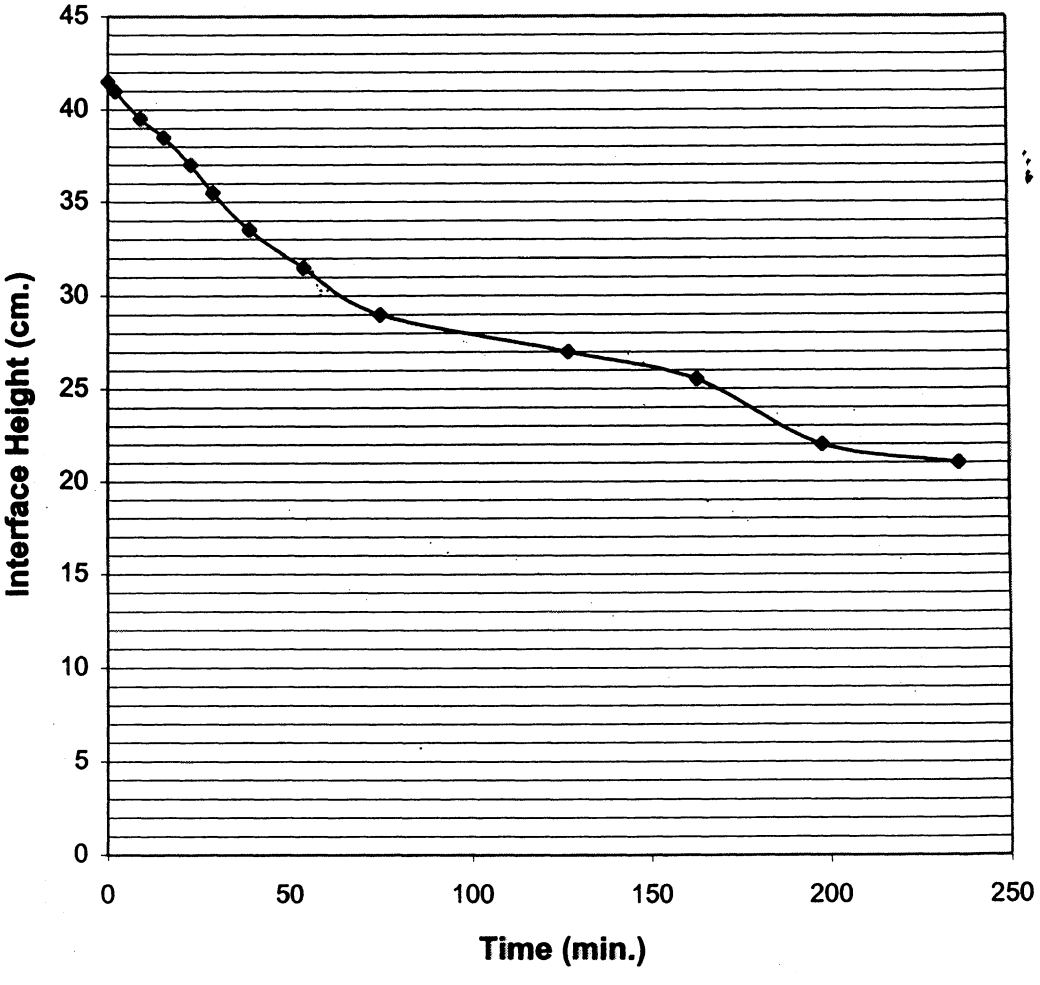

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Fig. 7 - Settling Rates (10XMn)

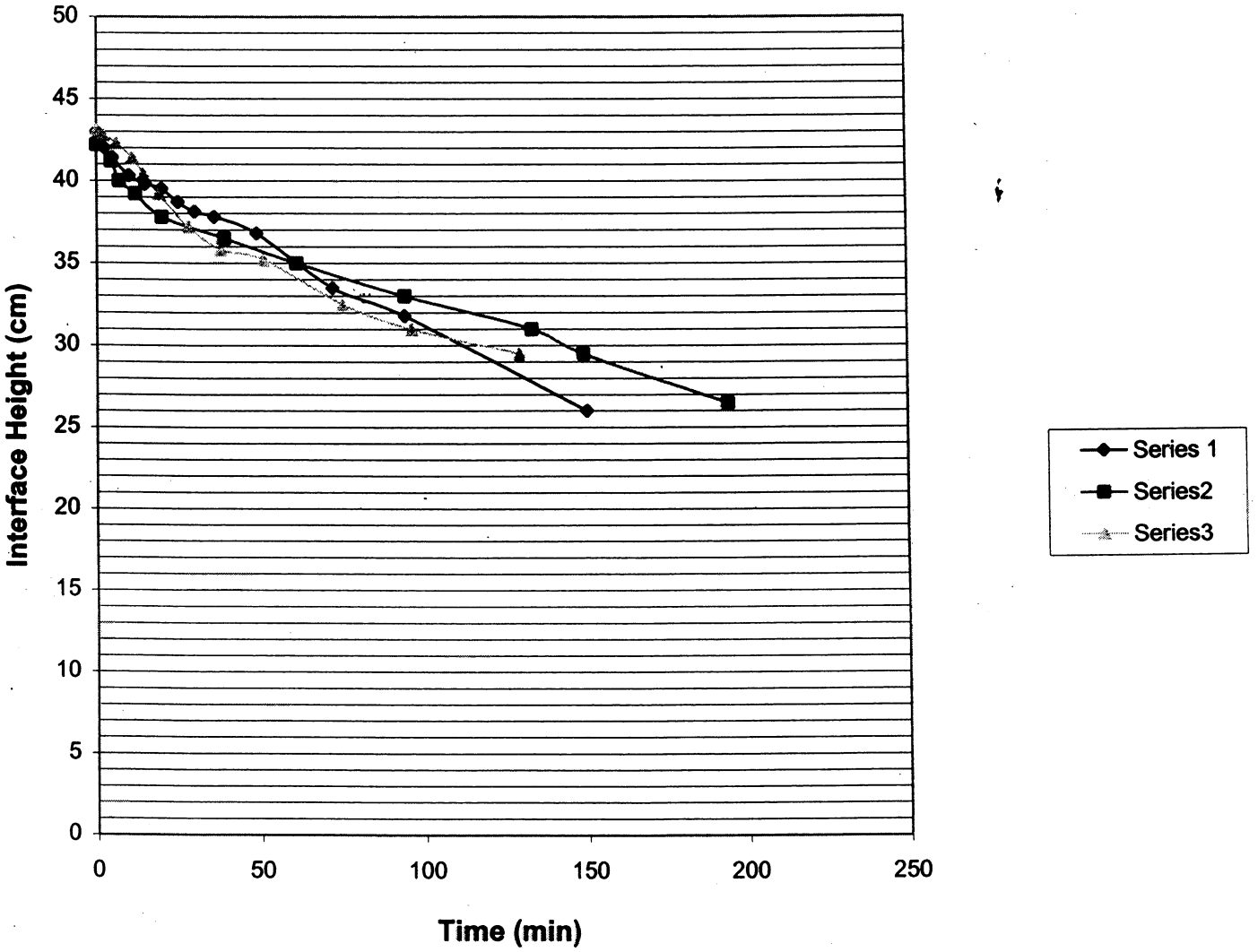

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Fig. 8 - Settling Rate (10XAl)

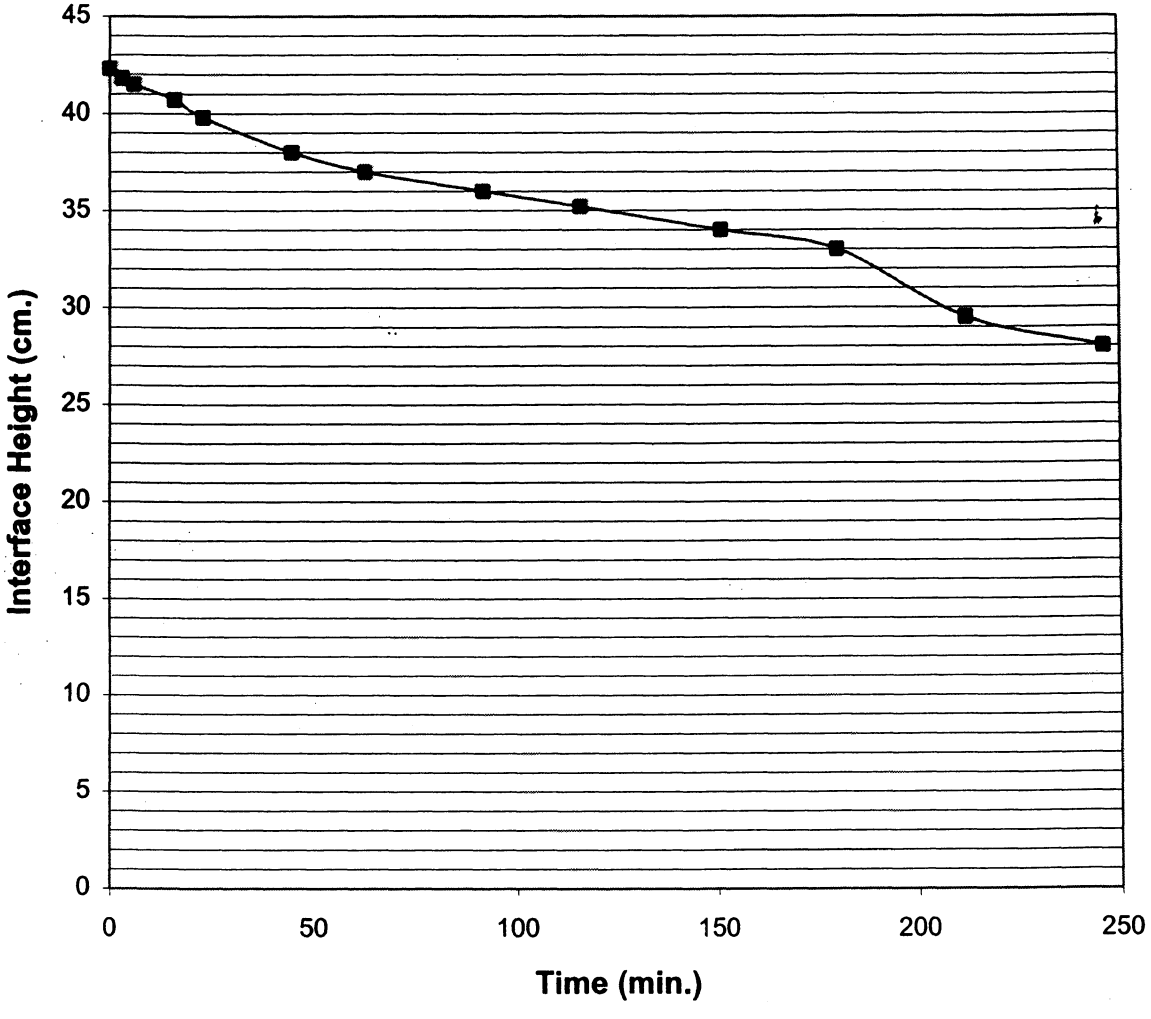

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Fig. 9 - Settling Rate (5XSi)

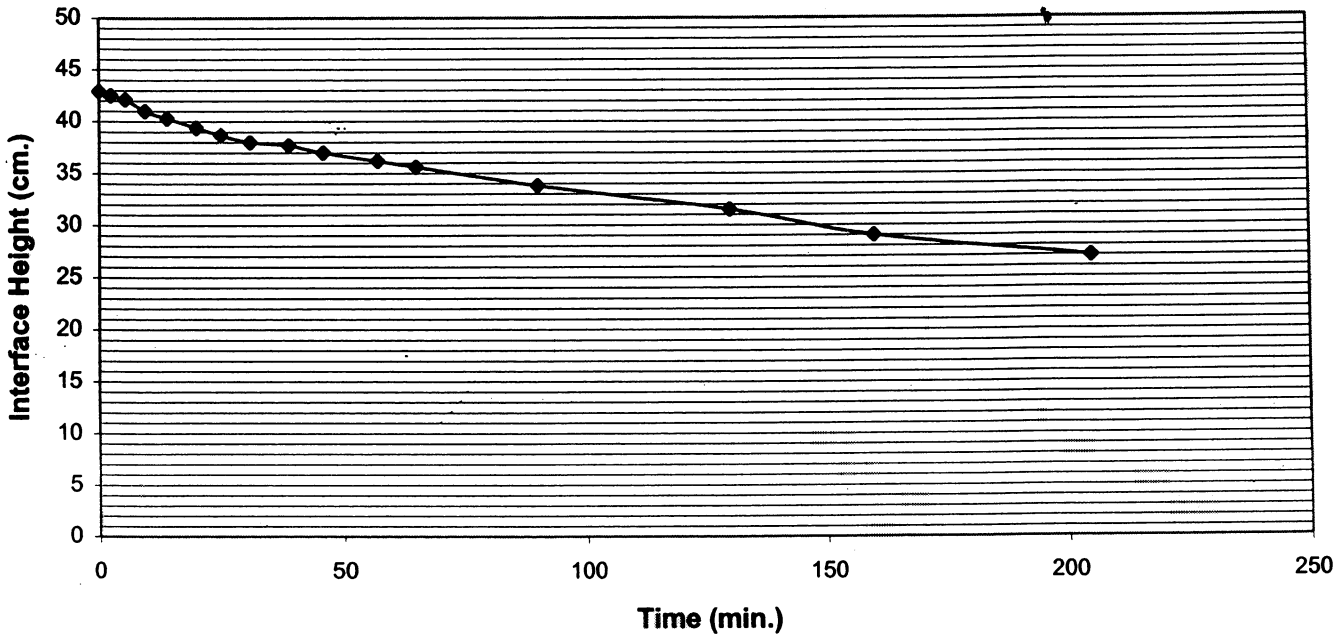

Fig. 10 - Settling Rate (10XCa)

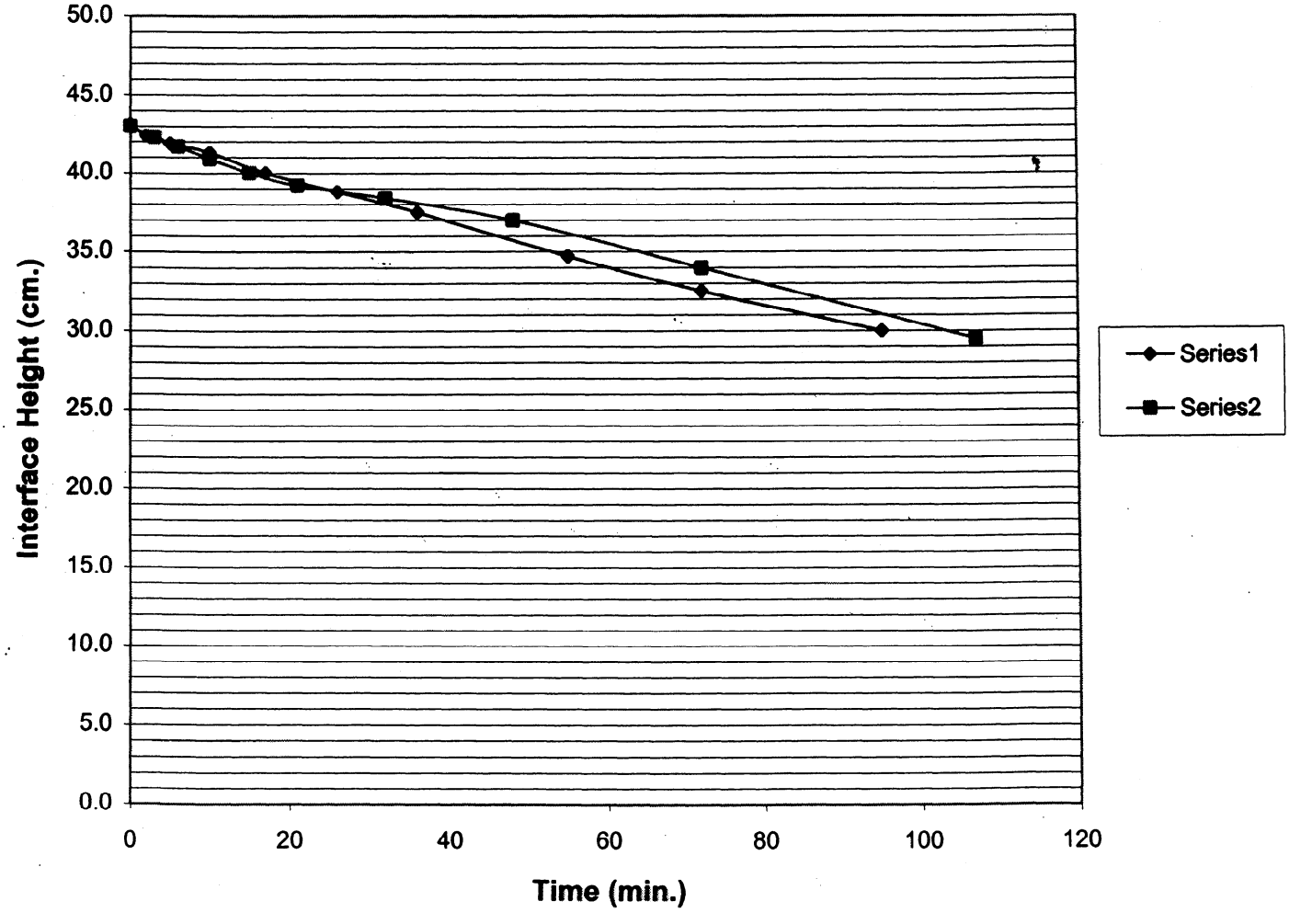

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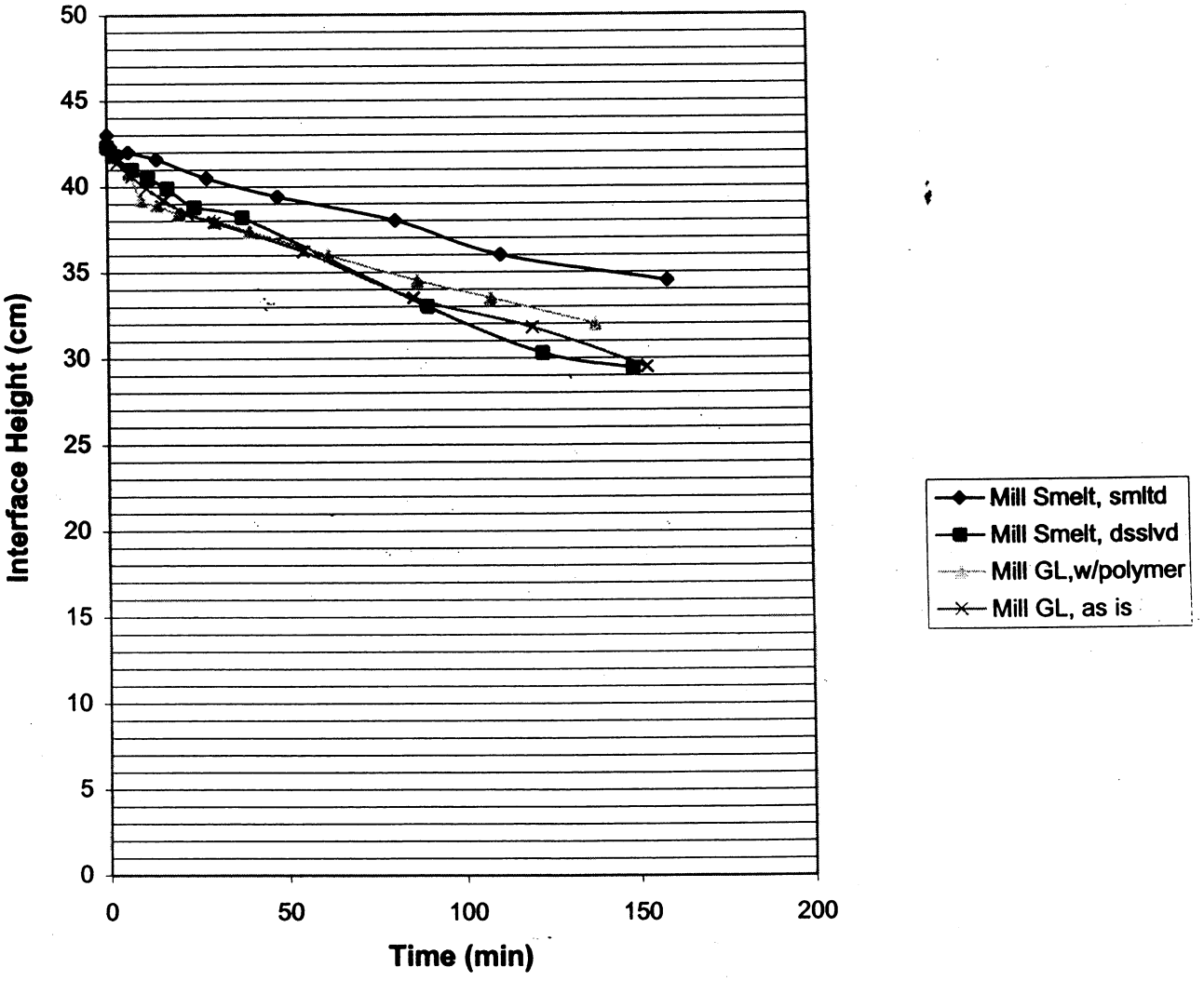
Fig.11 - Mill Settling Rates



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with high Mn is higher than the base at the 88% confidence level, while high Ca gives a lower time at only 79% confidence.

Qualitative comparison of the other (single) addback runs with the base case do suggest that high Al content will also result in a longer settling time and hence reduced performance. The run with mill smelt subjected to the laboratory smelting procedure (Run 093) also gave a high settling time, about double that for the same mill smelt dissolved in weak wash without prior "smelting" (Run 095). The cause for this is uncertain. The composition data reported above did show lower Fe in the mill dregs after "smelting" and a corresponding higher Fe in the clarified GL; the same dregs alsoshowed a much lower organic carbon content. Crystallographic and particle size differences will also have an impact and these will be discussed in the Microscopy Section below.

Some reassurance in the validity of the times reported in Table 9 is given by the mill green liquor, with (Run 100A) and without polymer settling aid (Run 100B) added. As expected, adding polymer lowered the calculated settling time.

Table 9. Calculated Dregs Settling Times for Continuous Clarifier

Run No.	Type	Time (min.)	Effect
040	Base	288, 329	-
045	Fe x 10	432, 453	high
049	Mg x 10	311	-
053	Mn x 10	315, 393	-
057	Al x 10	520	high
083	Si x 5	326	-
090	Ca x 10	278, 249	-
092	Mg x 10	n.a.	
093	Mill, smelted	534	high
095	Mill, dissolved	265	-
100A	Mill GL w/Poly	281	-
100B	Mill GL w/o Poly	367	-

4.4 Dregs Filtration Rates

From the differential form of Darcy's Law, it is shown in Appendix B that the cake permeability can be calculated from:

$$K = -\frac{\mu_f L}{\rho g t} \ln[(h_o + P_v/\rho g)/(h + P_v/\rho g)]$$

where the fluid properties, μ_f and ρ, are for clarified green liquor (CGL), h_o and h are the CGL heights in the settling column at time 0 and t, respectively, L is the cake thickness,

and P_v is the degree of vacuum. If the three constants in front of the ln-term are combined as $1/\alpha$, then

$$\alpha K \frac{t}{L} = \ln[(h_o + P_v/\rho g)/(h + P_v/\rho g)]$$

The parameter, L, is pressure dependent due to expected compaction at higher pressures.

A linear least squares fit to the liquid column height vs. time data gave filter cake permeabilities (actually α K) for two different downstream pressures, namely 5 and 8.5 in.Hg vacuum. In all cases, the coefficient of variation was >0.99. Results are shown in Table 10. The constant, α, is the product of green liquor density and the gravitational constant , divided by the liquor viscosity.

Table 10. Dregs Filter Cake Permeability Coefficients (K)

Run No.	Type	αK_5	$\alpha K_{8.5}$
40	Base	0.0032	0.0100
45	Fe x 10	0.0009	0.0010
49	Mg x 10	n.a.	n.a.
53	Mn x 10	0.0038	0.0101
57	Al x 10	0.0093	0.0270
83	Si x 5	0.0011	0.0035
90	Ca x 10	0.0051	0.0155
92	Mg x 10	0.0031	0.0074
93	Mill, smelted	0.0027	0.0067
95	Mill, dissolved	0.0018	0.0040
100A	Mill GL w/Poly	0.0009	0.0007
100B	Mill GL, as is	0.0016	0.0016

Unfortunately, time and budget limitations precluded carrying out duplicate runs, so an estimate of experimental error is not possible. Some qualitative observations can be made, however. Relative to the Base Case, the Mn, Mg, and Ca addbacks, plus the heat treated mill smelt, gave essentially the same permeabilities; Al was higher, while Fe, Si, Mill smelt (dissolved), and the Mill GL's were lower.

Surprisingly, the permeability coefficients for the runs using laboratory chemicals (except Fe) and mill smelt were higher for the higher ΔP's ($K_{8.5} > K_5$), whereas the mill green liquor (both with and without polymer added) and the Fe addback run did not show any pressure dependence. The expectation from a physical standpoint is that a higher ΔP should compress the cake more, reducing its void fraction. In general, cake thicknesses were 5-10% lower at the higher vacuum. The permeability (K) is dependent upon cake

void fraction (ε), surface area/volume of particles (S_o), and a constant, β, encompassing surface roughness and cake tortuosity as shown below (13):

$$K = \frac{\varepsilon^3}{\beta S_o^2 (1-\varepsilon)^2}$$

It can be shown mathematically that K should decrease as ε decreases; hence K would be expected to decrease as ΔP increased and ε decreased. The data do not support this expectation. Since tortuosity and surface roughness should not change with ΔP, then S_o must have decreased at the higher vacuum condition. One physical phenomenon that would give a smaller S_o would be removal of additional cake fines at the higher vacuum. Qualitatively, this was supported by visual observation of small amounts of fines in the filtrates collected.

Another inconsistency is seen in the relative behavior of the Mill green liquors, *as is* and with polymer added. With polymer added (Run 100A), the permeability is lower, which is the opposite of what would result from particles agglomerating and having a reduced S_o. This would suggest that the addition of polymer resulted in a lower void fraction in the filter cake. Unfortunately, this was not measured due to time and budget constraints.

4.5 Microscopy Results

Separation and characterization of particles in the green liquor samples was performed using filtration, microscopy, elemental analysis, and size measurement, all under the supervision and responsibility of David Rothbard. After mixing each sample, 50 mL was poured through a 20 μm (635 mesh) stainless steel sieve. The +20 μm particles were washed, dried, and collected on glass slides for size measurement and on carbon stubs for elemental analysis. After screening out the +20 μm fraction, a 10% dilution of the liquor was pulled through a 0.45 μm Metricel filter to form a filter cake of the solids. This filter cake should be representative of the "fines" fraction of the dregs. Accordingly, the cake was subjected to bulk EDS (energy dispersive x-ray spectroscopy) analysis to look at elemental spectra and imaged by SEM (scanning electron microscopy) for bulk texture. The SEM used was a JEOL JSM-6400 with a Link exL EDS system.

Results are summarized below in Table 11 for the longest linear dimension (LLD) for the two size fractions, as well as the weight per cent (of the initial green liquor sample) of the +20 μm fraction (at 3000X magnification) (Absolute weight percents of total dregs are not available.). The weight per cent data suggest the Fe and Al addbacks, and the mill smelt and mill green liquor samples to have significantly lower amounts of the +20 μm particles than the base run, whereas the Ca addback had a higher amount. These findings are all consistent with the settling rate results and with the permeability coefficient results (except for the Al case). The LLD results show no significant departures from the base case.

Why the smelted mill smelt (Run 093) had slower settling dregs than mill smelt just dissolved without lab smelting (Run 095) is hard to explain, Table 11 might suggest that the lower fraction of +20μm particles in Run 093 would imply a greater number of fines (<20μm), giving a lower settling rate; unfortunately, no more detailed particle size data are available.

The magnified images of the +20μm dregs particles showed some qualitative change from run to run. Relative to the base case, the Fe and Si addbacks (Runs 045 and 083) and the mill green liquor (Run 100) showed the presence of some "flaky" (as in corn flakes) particles, which might offer an increased resistance to flow of fluid past them; this could explain why these runs gave reduced permeabilities relative to the base case. Run 100 also showed the presence of more cubic like particles (characteristic of carbonates) and fewer fines.

Table 11. Dregs Fines Particle Size (μm)

Run No.	NPE	Mean Wt.% >20μm	Longest Linear Dimension (Std. Dev.) >20μm	<20μm
040	Base	0.21	18.2 (11.3)	1.07 (0.64)
045	Fe	0.08	17.7 (17.6)	0.86 (0.56)
049	Mg	0.17	27.1 (19.3)	1.02 (0.61)
053	Mn	0.24	23.3 (23.7)	1.57 (0.92)
057	Al	0.06	26.1 (19.2)	1.33 (1.17)
083	Si	0.26	17.8 (9.2)	1.58 (0.90)
090	Ca	0.53	20.0 (11.2)	2.02 (3.07)
093	Mill (sm)	0.02	20.6 (13.2)	1.62 (1.05)
095	Mill (dslv)	0.07	21.9 (12.6)	1.95 (1.11)
100	Mill GL	0.03	21.9 (13.0)	2.47 (1.66)

Table 12 summarizes EDS results for the <20 μm particles. These spectra can be compared with one another to look at relative amounts of elements present. Within a single spectrum, the fact that one peak is less intense than a nearby peak does not necessarily mean there is less of the former than the latter. Nonetheless, in most cases the NPE added back shows as the most intense peak (discounting sulfur) (most intense = 1, least intense = 8). The notable exceptions are Al and Si; recall that the partition coefficient results in Table 5 showed Al and Si to favor the green liquor over the dregs.

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Table 12. Relative X-Ray Peak Intensity of <20 μm Fraction

Run No.	NPE	Na	Mg	Al	Si	S	Ca	Mn	Fe.
040	Base	8	2	3	7	1	6	4	5
045	Fe	7	4	8	6	1	3	5	[redacted]
049	Mg	n.d.	[redacted]	7	3	4	2	6	5
053	Mn	8	4	7	3	2	5	[redacted]	6
057	Al	8	1	[redacted]	3	2	7	4	6
083	Si	8	1	6	[redacted]	2	7	4	5
090	Ca	n.d.	5	7	6	2	[redacted]	3	4
093	Mill(sm)	8	1	6	4	3	2	7	5
095	Mill(dslv)	8	1	2	4	3	7	6	5
100	Mill GL	n.d.	1	4	6	2	7	3	5

5.0 CONCLUSIONS

Composition

1. Each NPE addback laboratory run showed an elevated level of the NPE added in the dregs charge for that run. The high Mg runs represent the only case for judging experimental reproducibility in the green liquor dregs formed; agreement was generally within a factor of two.

2. Starting with mill smelt, NPE concentrations in dregs and the clarified green liquors, heat treated or not, were nearly identical, respectively. The only exception was organic carbon in the dregs where heat treatment resulted in a lower value, probably due to gasification and/or reduction reactions. NPE concentrations in clarified green liquors from mill smelt and from mill green liquor are nearly identical. Dregs from mill green liquor, with and without addition of polymer during clarification, were the same.

3. NPE concentrations in laboratory green liquors are within a factor of two vs. mill green liquors. Aluminum concentrations in laboratory green liquors are generally higher than in mill green liquors.

4. Partition coefficient results showed that Ca, Fe, Mg, and Mn would be removed effectively by the dregs – even if their concentrations in the liquor cycle increased. Partition coefficients for Si were uniformly low while Al partitions evenly between dregs and green liquor; hence removal of Si and Al from a closed liquor cycle must be by some method other than dregs removal.

Settling/Filtration Rate

5. Settling rate curves showed poor reproducibility within the four conditions where duplicates were run. The Fe and Al addbacks exhibited poor settling characteristics, while Mg and Ca gave the highest settling rates.

6. Statistical comparison of three addback NPE runs with the base case was made using a method which determines the hypothetical time to reach 10% solids underflow concentration in a continuous green liquor clarifier. Higher clarification times were given by the Fe addback at 98% confidence and Mn at 88%; Ca gave a lower time at the 79% confidence level. Qualitatively, Al also gave a higher settling time. Microscopic particle size analysis showed the Fe addback to have a greater fraction of small particles (<20μm), which would explain a lower settling rate; it also showed Ca to have a greater fraction of large particles (>20μm), resulting in a higher settling rate.

7. Mill smelt heat treated in the lab gave green liquor dregs which settled slower than the same mill smelt just dissolved in synthetic weak wash. Addition of polymer settling aid to raw mill green liquor lowered the calculated settling time relative to no polymer addition.

8. Filter cake permeability coefficients for the Mn, Mg, and Ca addbacks and heat treated mill smelt were the same as for the base case; Al was higher while Fe, Si, Mill Smelt (Dissolved), and the Mill Green Liquors were lower. Microscopic analysis of the filter cakes showed the Fe, Si, Mill Smelt (Dissolved), and Mill Green Liquors to have a greater fraction of small particles (<20μm), which should result in decreased the permeability coefficients due to relatively high specific surface areas.

9. Permeability coefficients increased at higher vacuum (i.e. higher ΔP), contrary to expectation. Removal of cake fines at higher vacuum resulting in a reduced surface area per unit volume is a plausible explanation.

10. Mill closed cycle operation must anticipate problems with buildup of Si, Al, and Fe in the liquor cycle due to unfavorable partition coefficients and/or settling rates in the green liquor clarifier.

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Appendix A – Mass Balance Data

Run No. 40

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3			0.706	-	153.210
Na2S			0.235	-	69.265
Na2SO4			0.020	-	3.158
NaCl			0.020	-	3.833
Dregs			0.020	-	-
	CaCO3		-	0.649	2.593
	Fe2O3		-	0.035	0.243
	Mg(OH)2		-	0.125	0.521
	MnO2		-	0.060	0.377
	SiO2		-	0.100	0.468
	Al2O3		-	0.010	0.054
	C		-	0.020	-
Total Solids		499.983	1	1.000	233.725
Xtln H2O		244			
Total Charge		743.983			
Product Smelt					
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt.M(g.)
NaOH	74.6	42.895
H2O	2910.4	0.000
Totals	2985	42.895

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = 0.847)

Component	g.Na_2O/ L	mg./kg.	g.	g. M
Na2CO3	70.7		365.570	158.644
Na2S	40.8		155.239	91.551
NaOH	13.2		51.512	29.619
NaCl		2900.28	10.356	4.072
Na2S2O3		10608.57	37.880	11.028
Na2SO4		5709.58	20.387	6.604
Ca		10.6	0.038	0.038
Fe		0.366	0.001	0.001
Mg		2.12	0.008	0.008
Mn		0.094	0.000	0.000
Si		145	0.518	0.518
Al		37.4	0.134	0.134
C		0	0.000	0.000

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Chloride		[illegible]	6.284	0.000
SO4		[illegible]	13.783	0.000
S2O3		[illegible]	26.852	0.000
Totals	124.7	21174.02	641.642	302.217

Total Clarified GL (g.)=	3570.7

Dregs

Component	Wt.fr.	g.	g.M
Ca	[illegible]	1.413	1.413
Fe		0.170	0.170
Mg		0.305	0.305
Mn		0.249	0.249
Si		0.034	0.034
Al		0.057	0.057
Na		1.085	1.085
C		0.000	0.000
Total Dregs (g.) =			3.311

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na	272.363	302.603	1.111	0.00	99.64
Ca	2.5932	1.45	0.559	37.32	2.61
Fe	0.243	0.171	0.702	129.70	0.77
Mg	0.521	0.313	0.600	40.30	2.42
Mn	0.377	0.249	0.660	740.66	0.13
Si	0.468	0.552	1.178	0.07	93.85
Al	0.054	0.190	3.519	0.42	70.27
Totals	276.620	305.527	1.105		

Total Green Liquor Solids in	671.6
Total Green Liquor Solids Out	652.9
GL Solids Closure	0.972

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Run No. [redacted]

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt.M (g.)
Na2CO3		[redacted]	0.701	-	152.191
Na2S			0.233	-	68.847
Na2SO4			0.019	-	3.142
NaCl			0.019	-	3.814
Dregs		13.155	0.026	-	-
	CaCO3	[redacted]	-	0.494	2.600
	Fe2O3		-	0.266	2.449
	Mg(OH)2		-	0.095	0.521
	MnO2		-	0.046	0.379
	SiO2		-	0.076	0.468
	Al2O3		-	0.008	0.053
	C		-	0.015	-
Total Solids		499.995		1.000	234.464
Xtln H2O		[redacted]			
Total Charge		742.495			
Product Smelt =		[redacted]			
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	[redacted]	42.263
H2O		0.000
Totals	2942	42.263

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = [redacted])

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	[redacted]		360.673	156.519
Na2S			152.568	89.976
NaOH			48.059	27.634
NaCl		2010.42	7.098	2.791
Na2S2O3		7505.00	26.496	7.714
Na2SO4		8076.25	28.512	9.236
Ca		[redacted]	0.038	0.038
Fe			0.000	0.000
Mg			0.010	0.010
Mn			0.000	0.000
Si			0.911	0.911
Al		18.5	0.065	0.065
C		0	0.000	0.000
Chloride		1218	4.307	0.000
SO4		5460	19.276	0.000
S2O3		5320	18.782	0.000
Totals	124	19101.91	624.431	294.894

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Total Clarified GL (g.)= 3530.4

Dregs

Component	Wt.fr.	g.	g.M
Ca		0.000	0.000
Fe		0.000	0.000
Mg		0.000	0.000
Mn		0.000	0.000
Si		0.000	0.000
Al		0.000	0.000
Na		0.000	0.000
C		0.000	0.000
Total Dregs (g.) =			0.000

Mass Balances

Component	M in (g.)	M out (g.)	Closure
Na	270.256	293.869	1.087
Ca	2.6004	0.04	0.015
Fe	2.449	0.000	0.000
Mg	0.521	0.010	0.018
Mn	0.379	0.000	0.001
Si	0.468	0.911	1.948
Al	0.053	0.065	1.221
Totals	276.727	294.894	1.066

Total Green Liquor Solids in	661.9
Total Green Liquor Solids Out	624.4
GL Solids Closure	0.943

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Run No. 49

Input Smelt Chemicals

Component	Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3	344.8	0.690	-	149.630
Na2S	[illegible]	0.230	-	67.697
Na2SO4	[illegible]	0.019	-	3.094
NaCl	[illegible]	0.019	-	3.755
Dregs	21.253	0.043	-	-
CaCO3	[illegible]	-	0.306	2.600
Fe2O3	[illegible]	-	0.017	0.246
Mg(OH)2	[illegible]	-	0.588	5.210
MnO2	[illegible]	-	0.028	0.379
SiO2	[illegible]	-	0.047	0.468
Al2O3	[illegible]	-	0.005	0.053
C	0.2	-	0.009	-
Total Solids	499.943	1	1.000	233.131
Xtln H2O	[illegible]			
Total Charge	738.343			
Product Smelt	[illegible]			
Smelt to GL	[illegible]			

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	[illegible]	42.838
H2O	2906	0.000
Totals	2980.5	42.838

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = [illegible])

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	73.8		370.426	160.751
Na2S	47.3		174.701	103.029
NaOH	17.8		67.429	38.772
NaCl		2125.77	7.574	2.978
Na2S2O3		9451.79	33.676	9.804
Na2SO4		5339.79	19.025	6.163
Ca		[illegible]	0.047	0.047
Fe		[illegible]	0.000	0.000
Mg		27	0.010	0.010
Mn		0.083	0.000	0.000
Si		127	0.452	0.452
Al		1.29	0.005	0.005
C		0	0.000	0.000
Chloride		1290	4.596	0.000
SO4		3610	12.862	0.000
S2O3		6700	23.871	0.000
Totals	138.9	18351.76	673.345	322.011

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Total Clarified GL (g.)= 3562.9

Dregs

Component	Wt.fr.	g.	g.M
Ca	0.107	1.466	1.466
Fe	0.012	0.164	0.164
Mg	0.193	2.644	2.644
Mn	0.018	0.247	0.247
Si	0.003	0.044	0.044
Al		0.060	0.060
Na		2.637	2.637
C		0.000	0.000
Total Dregs (g.) =			7.262

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na	267.013	324.134	1.214	0.01	99.19
Ca	2.6004	1.51	0.582	31.17	3.11
Fe	0.246	0.165	0.672	354.94	0.28
Mg	5.210	2.654	0.509	274.86	0.36
Mn	0.379	0.247	0.651	833.89	0.12
Si	0.468	0.496	1.062	0.10	91.17
Al	0.053	0.065	1.213	13.12	7.08
Totals	275.969	329.274	1.193		

Total Green Liquor Solids in	670.6
Total Green Liquor Solids out	687.0
GL Solids Closure	1.025

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Run No. 53

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3		349	0.698	-	151.453
Na2S			0.232	-	68.528
Na2SO4			0.019	-	3.126
NaCl			0.019	-	3.794
Dregs			0.031	-	-
	CaCO3		-	0.422	2.598
	Fe2O3		-	0.023	0.247
	Mg(OH)2		-	0.081	0.521
	MnO2		-	0.390	3.790
	SiO2		-	0.065	0.468
	Al2O3		-	0.007	0.053
	C		-	0.013	-
Totals			1	1.000	234.579
Xtln H2O					
Total Charge		741.3			
Product Smelt	Smelt =				
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	75.4	43.355
H2O	2939.6	0.000
Totals	3015	43.355

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = 0.837)

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	70.8		365.088	158.434
Na2S	48.8		166.198	98.014
NaOH	19.6		76.279	43.860
NaCl		2224.65	8.017	3.152
Na2S2O3		9987.86	35.991	10.478
Na2SO4		4319.17	15.564	5.042
Ca		9.8	0.035	0.035
Fe		0.2	0.001	0.001
Mg		1.75	0.006	0.006
Mn		0.124	0.000	0.000
Si		415	1.495	1.495
Al		24	0.086	0.086
C		0	0.000	0.000
Chloride		1350	4.865	0.000
SO4		2920	10.522	0.000
S2O3		7080	25.513	0.000

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Totals	134.2	18332.75	668.763	320.607
Total Clarified GL (g.)=		3603.5		

Dregs

Component	Wt.fr.	g.	g.M
Ca		1.436	1.436
Fe		0.218	0.218
Mg		0.377	0.377
Mn		3.190	3.190
Si		0.015	0.015
Al		0.058	0.058
Na		0.522	0.522
C		0.015	0.000
Total Dregs (g.) =			5.815

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na	270.256	319.503	1.182	0.00	99.84
Ca	2.5976	1.47	0.566	40.65	2.40
Fe	0.247	0.219	0.887	150.14	0.66
Mg	0.521	0.383	0.735	59.78	1.65
Mn	3.790	3.190	0.842	7139.12	0.01
Si	0.468	1.510	3.223	0.01	99.04
Al	0.053	0.144	2.702	0.67	59.86
Totals	277.934	326.421	1.174		

Total Green Liquor Solids in	678.4
Total Green Liquor Solids out	683.3
GL Solids Closure	1.007

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Run No. [redacted]

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3		[redacted]	0.705	-	152.885
Na2S			0.235	-	69.177
Na2SO4			0.019	-	3.158
NaCl			0.019	-	3.833
Dregs		10.913	0.022	-	-
	CaCO3	[redacted]	-	0.596	2.600
	Fe2O3		-	0.032	0.243
	Mg(OH)2		-	0.115	0.524
	MnO2		-	0.055	0.380
	SiO2		-	0.092	0.470
	Al2O3		-	0.092	0.530
	C		-	0.018	-
Totals		500.013	1	1.000	233.801
Xtln H2O		[redacted]			
Total Charge		743.613			
Product Smelt		[redacted]			
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	[redacted]	44.908
H2O		0.000
Totals	3124	44.908

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = [redacted])

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	[redacted]		386.350	167.661
Na2S			166.860	98.405
NaOH			67.320	38.709
NaCl		2290.56	8.520	3.350
Na2S2O3		8407.86	31.273	9.105
Na2SO4		6020.21	22.392	7.254
Ca		[redacted]	0.036	0.036
Fe			0.013	0.013
Mg			0.007	0.007
Mn			0.000	0.000
Si			0.722	0.722
Al			0.311	0.311
C			0.000	0.000
Chloride			5.170	0.000
SO4			15.138	0.000
S2O3			22.168	0.000

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Totals	130.7	18401.34	683.803	325.572
Total Clarified GL (g.)=		3719.47		

Dregs

Component	Wt.fr.	g.	g.M
Ca		1.526	1.526
Fe		0.241	0.241
Mg		0.466	0.466
Mn		0.337	0.337
Si		0.008	0.008
Al		0.104	0.104
Na		0.161	0.161
C		0.031	0.000
Total Dregs (g.) =			2.843

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na	273.961	324.644	1.185	0.00	99.95
Ca	2.6	1.56	0.601	42.51	2.30
Fe	0.243	0.254	1.047	18.09	5.24
Mg	0.524	0.473	0.902	67.68	1.46
Mn	0.380	0.338	0.888	686.93	0.15
Si	0.470	0.730	1.551	0.01	98.90
Al	0.530	0.415	0.783	0.34	74.84
Totals	278.708	328.415	1.178		

Total Green Liquor Solids in	681.6
Total Green Liquor Solids out	691.8
GL Solids Closure	1.015

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Run No. 83

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt.M (g.)
Na2CO3		350.2	0.700	-	151.974
Na2S			0.233	-	68.705
Na2SO4			0.019	-	3.136
NaCl			0.019	-	3.774
Dregs		14.007	0.028	-	-
	CaCO3		-	0.464	2.602
	Fe2O3		-	0.025	0.247
	Mg(OH)2		-	0.089	0.522
	MnO2		-	0.043	0.378
	SiO2		-	0.357	2.335
	Al2O3		-	0.007	0.055
	C	0.2	-	0.014	-
Totals		499.987	1	1.000	233.728
Xtln H2O					
Total Charge		742.087			
Product Smelt					
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	76.6	44.045
H2O	2985.9	0.000
Totals	3062.5	44.045

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = 0.845 est.

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	84		338.642	146.958
Na2S	47.6		185.334	109.300
NaOH	17.3		69.086	39.725
NaCl		1911.55	7.001	2.753
Na2S2O3		9465.89	34.670	10.094
Na2SO4		12735.63	46.646	15.111
Ca		16.6	0.061	0.061
Fe		0.8	0.003	0.003
Mg		2.2	0.008	0.008
Mn		0.115	0.000	0.000
Si		469	1.718	1.718
Al		13.5	0.049	0.049
C		0	0.000	0.000
Chloride		1160	4.249	0.000
SO4		8610	31.535	0.000
S2O3		6710	24.576	0.000
Totals	128.9	25775.26	683.218	325.778

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Total Clarified GL (g.)= 3662.6

Dregs

Component	Wt.fr.	g.	g.M
Ca	[illegible]	2.294	2.294
Fe	[illegible]	0.397	0.397
Mg	0.048	0.595	0.595
Mn	0.04	0.496	0.496
Si	[illegible]	0.016	0.016
Al	[illegible]	0.161	0.161
Na	[illegible]	0.248	0.248
C	[illegible]	0.092	0.000
Total Dregs (g.) =			4.207

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na	271.634	324.187	1.193	0.00	99.92
Ca	2.6024	2.35	0.905	37.73	2.58
Fe	0.247	0.400	1.619	135.25	0.73
Mg	0.522	0.603	1.155	74.54	1.32
Mn	0.378	0.496	1.314	1177.59	0.08
Si	2.335	1.734	0.743	0.01	99.07
Al	0.055	0.211	3.863	3.26	23.47
Totals	277.773	329.986	1.188		

Total Green Liquor Solids in	689.1
Total Green Liquor Solids out	695.6
GL Solids Closure	1.009

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Run No. [redacted]

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3		[redacted]	0.622	-	134.875
Na2S			0.207	-	60.979
Na2SO4			0.017	-	2.789
NaCl			0.017	-	3.379
Dregs		68.544	0.137	-	-
	CaCO3		-	0.948	25.990
	Fe2O3		-	0.005	0.243
	Mg(OH)2		-	0.018	0.523
	MnO2		-	0.009	0.390
	SiO2		-	0.015	0.480
	Al2O3		-	0.002	0.061
	C		-	0.003	-
Totals		499.948	1	1.000	229.711
Xtln H2O		[redacted]			
Total Charge		714.848			
Product Smelt		[redacted]			
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	[redacted]	42.320
H2O		0.000
Totals	2945	42.320

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = [redacted] est.

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	[redacted]		379.164	164.543
Na2S			128.916	76.027
NaOH			55.251	31.769
NaCl		1779.72	6.205	2.440
Na2S2O3		9113.21	31.773	9.250
Na2SO4		14436.67	50.333	16.305
Ca		[redacted]	0.067	0.067
Fe			0.003	0.003
Mg			0.007	0.007
Mn			0.000	0.000
Si			1.911	1.911
Al			0.096	0.096
C			0.000	0.000
Chloride			3.765	0.000
SO4		9760	34.028	0.000
S2O3		6460	22.523	0.000

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Totals	124.3	27007.33	653.726	302.418
Total Clarified GL (g.)=		3486.5		

Dregs

Component	Wt.fr.	g.	g.M
Ca	[redacted]	18.668	18.668
Fe		0.223	0.223
Mg		0.418	0.418
Mn		0.309	0.309
Si		0.038	0.038
Al		0.038	0.038
Na		0.143	0.143
C		0.024	0.000
Total Dregs (g.) =			19.836

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na	244.343	300.477	1.230	0.00	99.95
Ca	25.99	18.73	0.721	278.87	0.36
Fe	0.243	0.226	0.929	78.09	1.26
Mg	0.523	0.425	0.813	57.92	1.70
Mn	0.390	0.309	0.792	641.71	0.16
Si	0.480	1.949	4.062	0.02	98.05
Al	0.061	0.134	2.199	0.40	71.62
Totals	272.031	322.254	1.185		

Total Green Liquor Solids in	662.6
Total Green Liquor Solids out	701.2
GL Solids Closure	1.058

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Run No. [redacted]

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3		[redacted]	0.689	-	149.674
Na2S			0.230	-	67.791
Na2SO4			0.019	-	3.097
NaCl			0.019	-	3.759
Dregs		21.285	0.043	-	-
	CaCO3	[redacted]	-	0.305	2.594
	Fe2O3		-	0.016	0.243
	Mg(OH)2		-	0.589	5.224
	MnO2		-	0.029	0.387
	SiO2		-	0.047	0.466
	Al2O3		-	0.005	0.052
	C		-	0.010	-
Totals		500.255	1	1.000	233.287
Xtln H2O		[redacted]			
Total Charge		738.955			
Product Smelt		[redacted]			
Smelt to GL		608			

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	[redacted]	43.700
H2O		0.000
Totals	3040	43.700

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = [redacted] est.

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	[redacted]		386.447	167.703
Na2S			193.921	114.364
NaOH			53.064	30.512
NaCl		2092.82	7.590	2.984
Na2S2O3		14530.36	52.695	15.342
Na2SO4		24554.17	89.047	28.846
Ca		[redacted]	0.072	0.072
Fe			0.003	0.003
Mg			0.010	0.010
Mn			0.001	0.001
Si		413	1.498	1.498
Al		17	0.062	0.062
C		0	0.000	0.000
Chloride		1270	4.606	0.000
SO4		16600	60.201	0.000
S2O3		10300	37.353	0.000
Totals	138.3	42901.24	784.410	361.397

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Total Clarified GL (g.)= 3626.54

Dregs

Component	Wt.fr.	g.	g.M
Ca	[redacted]	1.652	1.652
Fe		0.279	0.279
Mg		4.743	4.743
Mn		0.365	0.365
Si		0.021	0.021
Al		0.236	0.236
Na		0.107	0.107
C		0.011	0.000
Total Dregs (g.) =			7.404

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na	268.020	359.858	1.343	0.00	99.97
Ca	2.5936	1.72	0.665	23.01	4.16
Fe	0.243	0.282	1.163	82.72	1.19
Mg	5.224	4.753	0.910	462.11	0.22
Mn	0.387	0.366	0.945	294.14	0.34
Si	0.466	1.519	3.259	0.01	98.59
Al	0.052	0.298	5.680	3.83	20.71
Totals	276.987	368.801	1.331		

Total Green Liquor Solids in	684
Total Green Liquor Solids out	805.9
GL Solids Closure	1.178

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Run No. [redacted]93

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3		[redacted]		-	
Na2S				-	
Na2SO4				-	
NaCl				-	
Dregs		0		-	
	CaCO3	[redacted]	-		
	Fe2O3		-		
	Mg(OH)2		-		
	MnO2		-		
	SiO2		-		
	Al2O3		-		
	C		-		
Totals		410			
Xtln H2O					
Total Charge		410			
Product Smelt		[redacted]			
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	[redacted]	29.181
H2O	1979.25	0.000
Totals	2030	29.181

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = [redacted] est.

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	[redacted]		272.223	118.135
Na2S			79.971	47.162
NaOH	16.9		44.860	25.794
NaCl		3262.82	7.943	3.123
Na2S2O3		8704.11	21.190	6.169
Na2SO4		16270.83	39.612	12.832
Ca		[redacted]	0.045	0.045
Fe			0.002	0.002
Mg			0.004	0.004
Mn			0.000	0.000
Si		200	0.487	0.487
Al		12.8	0.031	0.031
C		0	0.000	0.000
Chloride		1980	4.820	0.000
SO4		11000	26.780	0.000
S2O3		6170	15.021	0.000
Totals	125.2	30451.40	466.368	213.784

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Total Clarified GL (g.)= 2434.52

Dregs

Component	Wt.fr.	g.	g.M
Ca	[redacted]	0.114	0.114
Fe		0.019	0.019
Mg		0.327	0.327
Mn		0.025	0.025
Si		0.001	0.001
Al		0.016	0.016
Na		0.007	0.007
C		0.001	0.000
Total Dregs (g.) =			0.511

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na		213.223		0.00	100.00
Ca		0.16		2.56	28.11
Fe		0.021		8.68	10.33
Mg		0.331		90.17	1.10
Mn		0.026		71.77	1.37
Si		0.488		0.00	99.70
Al		0.047		0.52	65.68
Totals		214.295			

Total Green Liquor Solids in	456.75
Total Green Liquor Solids out	467.8
GL Solids Closure	1.024

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Run No. [redacted]

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3		[redacted]		-	
Na2S				-	
Na2SO4				-	
NaCl				-	
Dregs		0		-	
	CaCO3	[redacted]	-		
	Fe2O3		-		
	Mg(OH)2		-		
	MnO2		-		
	SiO2		-		
	Al2O3		-		
	C		-		
Totals		410			
Xtln H2O					
Total Charge					
Product	Smelt =	[redacted]			
Smelt to GL					

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH	[redacted]	29.469
H2O		0.000
Totals	2050	29.469

Products

Clarified Green Liquor

(Specific Volume (mL/g.) = [redacted] est.

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3	[redacted]		279.168	121.148
Na2S			83.634	49.322
NaOH			45.570	26.203
NaCl		3510.00	8.629	3.393
Na2S2O3		7617.86	18.729	5.453
Na2SO4		12972.29	31.893	10.331
Ca		[redacted]	0.041	0.041
Fe			0.001	0.001
Mg			0.004	0.004
Mn			0.000	0.000
Si			0.595	0.595
Al			0.030	0.030
C			0.000	0.000
Chloride			5.237	0.000
SO4			21.561	0.000
S2O3		5400	13.276	0.000
Totals	127.6	26503.40	468.294	216.522

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Total Clarified GL (g.)= 2458.51

Dregs

Component	Wt.fr.	g.	g.M
Ca	[redacted]	0.179	0.179
Fe		0.060	0.060
Mg		0.107	0.107
Mn		0.048	0.048
Si		0.005	0.005
Al		0.022	0.022
Na		0.107	0.107
C		0.102	0.000
Total Dregs (g.) =			0.528

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na		215.957		0.00	99.95
Ca		0.22		4.41	18.49
Fe		0.061		39.74	2.45
Mg		0.112		24.38	3.94
Mn		0.048		131.04	0.76
Si		0.600		0.01	99.13
Al		0.052		0.75	57.30
Totals		217.050			
Total Green Liquor Solids in		461.25			
Total Green Liquor Solids out		469.8			
GL Solids Closure		1.019			

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Run No. 100

Input Smelt Chemicals

Component		Wt.(g.)	Wt.fr.	wt.fr.	Wt. M (g.)
Na2CO3				-	
Na2S				-	
Na2SO4				-	
NaCl				-	
Dregs		0		-	
	CaCO3		-		
	Fe2O3		-		
	Mg(OH)2		-		
	MnO2		-		
	SiO2		-		
	Al2O3		-		
	C		-		
Totals					
Product	Smelt =				

Weak Wash Chemicals

Component	Wt. (g.)	Wt. M (g.)
NaOH		
H2O		
Totals		

Products

Clarified Green Liquor (Specific Volume (mL/g.) = est.

Component	g.Na2O/L	mg./kg.	g.	g. M
Na2CO3			119.029	51.654
Na2S			35.078	20.687
NaOH	4.1		4.497	2.586
NaCl		4202.11	4.227	1.662
Na2S2O3		10213.57	10.275	2.991
Na2SO4		19229.17	19.345	6.267
Ca			0.017	0.017
Fe			0.001	0.001
Mg			0.002	0.002
Mn			0.000	0.000
Si		174	0.175	0.175
Al		7.9	0.008	0.008
C		0	0.000	0.000
Chloride		2550	2.565	0.000
SO4		13000	13.078	0.000
S2O3		7240	7.283	0.000
Totals	118.8	36395.95	192.653	86.049

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Total Clarified GL (g.)= 1006

Dregs

Component	Wt.fr.	g.	g.M
Ca	[redacted]	0.033	0.033
Fe		0.016	0.016
Mg		0.044	0.044
Mn		0.020	0.020
Si		0.002	0.002
Al		0.010	0.010
Na		0.046	0.046
C		0.007	0.000
Total Dregs (g.) =			0.171

Mass Balances

Component	M in (g.)	M out (g.)	Closure	Part'n Coeff.(D/CGL)	%M in CGL
Na		85.893		0.00	99.95
Ca		0.05		1.99	33.41
Fe		0.016		25.01	3.84
Mg		0.046		22.61	4.23
Mn		0.020		353.67	0.28
Si		0.177		0.01	98.94
Al		0.018		1.24	44.58
Totals		86.220			

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Appendix B – Filter Cake Permeability (13)

Darcy's Law relates the flow of a fluid through a packed bed of particles to the total surface area of the particles and the pressure gradient through the bed. Kozeny later modified this equation to include the effects of fluid viscosity and bed porosity (i.e. void fraction):

$$Q = \frac{KA\Delta P}{\mu_f L}$$

where:

Q = volumetric flow rate through the bed
A = cross-sectional area of bed
L = bed thickness
ΔP = the fluid pressure drop across the bed
μ_f = viscosity of the fluid (measured to be 0.7 cP at 85°C).
K = permeability coefficient

The permeability coefficient is dependent upon the bed void fraction, the specific surface area of the particles, and the actual structure of the medium, including the tortuosity of the pores. It is expressed by:

$$K = \frac{\varepsilon^3}{\beta S_o^2 (1-\varepsilon)^2}$$

where:

ε = cake void fraction
S_o = surface area/volume of particles
β = constant containing various factors including cake tortuosity

If the Kozeny Eq. is expressed in differential form, the volumetric flow rate of a differential element of green liquor (A dh) with density ρ at height h in the column with a vacuum pressure P_v applied to the filtrate outlet is:

$$-A\, dh/dt = K A (\rho g h + P_v)/\mu_f L$$

Integration of this equation between the initial column height (h_o) and the height at time t yields:

$$K = \frac{\mu_f L}{\rho g t} \ln[(h_o + P_v/\rho g)/(h + P_v/\rho g)]$$

If the three constants in front of the ln-term are combined as $1/\alpha$, then

$$\alpha K \frac{t}{L} = \ln[(h_o + P_v/\rho g)/(h + P_v/\rho g)]$$

The parameter, L, is pressure dependent due to expected compaction at higher pressures.

Appendix C – Theoretical Equilibrium Smelt Compositions

Table C-1 : Smelt Formation at 800°C (New Base Case with High SiO_2)

SPECIES	Smelt In	Smelt In	Smelt Out	Smelt Out-In
Run 040	g.	wt.fr.	g.	g.
H2O	0	0		
Na2CO3	353.05	0.706111	354.36	1.31
NaHCO3	0	0	0.22	0.22
Na2S	117.45	0.234904	115.22	-2.23
Na2SO3	0	0	0.08	0.08
Na2SO4	9.749	0.019498	8.85	-0.899
NaCl	9.75	0.01952	9.75	-0.00
NaOH	0	0	1.54	1.54
CaCO3	6.483	0.012966	5.76	-0.723
Fe2O3	0.348	0.000696	0	-0.348
Mg(OH)2	1.251	0.002502	0.045	-1.206
MnO2	0.597	0.001194	0	-0.597
SiO2	1.002	0.002004	1.002	0.000
Al2O3	0.102	0.000204	0	-0.102
C	0.2	0.0004	0.1	-0.1
S		0	0.44	0.44
Ca(OH)2		0	0.01	0.01
MgO		0	0.81	0.81
NaAlO2		0	0.16	0.16
FeS		0	0.17	0.17
FeS2		0	0.27	0.27
MnS		0	0.58	0.58
CaS		0	0.5	0.5
FeO		0	0.01	0.01
MnO		0	0.015	0.015
MgCO3		0	0.03	0.03
TOTAL	499.992	1	499.92	-0.072

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Table C-2 : Smelt Formation at 800°C (Mg Content 10X)

SPECIES	Smelt In	Smelt In	Smelt Out	Smelt Out-In
Run 049	g.	wt.fr.	g.	g.
H2O	0	0		
Na2CO3	344.8	0.689683	342.27	-2.53
NaHCO3	0	0	1.11	1.11
Na2S	114.787	0.229602	108.72	-6.067
Na2SO3	0	0	0.08	0.08
Na2SO4	9.55	0.019102	8.95	-0.6
NaCl	9.55	0.019102	9.55	0
NaOH	0	0	7.78	7.78
CaCO3	6.501	0.013004	5.43	-1.071
Fe2O3	0.351	0.000702	0	-0.351
Mg(OH)2	12.5	0.025003	6.14	-6.36
MnO2	0.601	0.001202	0	-0.601
SiO2	0.999	0.001998	0.999	0
Al2O3	0.101	0.000202	0	-0.101
C	0.2	0.0004	0.44	0.24
S		0	1.95	1.95
Ca(OH)2		0	0.34	0.34
MgO		0	4.24	4.24
NaAlO2		0	0.16	0.16
FeS		0	0.17	0.17
FeS2		0	0.27	0.27
MnS		0	0.58	0.58
CaS		0	0.43	0.43
FeO		0	0.01	0.01
MnO		0	0.015	0.015
MgCO3		0	0.16	0.16
TOTAL	499.94	1	499.794	-0.146

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Table C-3 : Smelt Formation at 800°C (Mn Content 10X)

SPECIES	Smelt In	Smelt In	Smelt Out	Smlt Out-In
Run 053	g.	wt.fr.	g.	g.
H2O	0	0		
Na2CO3	349	0.698134	353.17	4.17
NaHCO3	0	0	0.003	0.003
Na2S	116.2	0.232445	110.67	-5.53
Na2SO3	0	0	0.09	0.09
Na2SO4	9.652	0.019308	10.91	1.258
NaCl	9.652	0.019308	9.652	0
NaOH	0	0	1.698	1.698
CaCO3	6.494	0.01299	4.345	-2.149
Fe2O3	0.353	0.000706	0	-0.353
Mg(OH)2	1.251	0.002502	0	-1.251
MnO2	5.999	0.012	0	-5.999
SiO2	1.002	0.002004	1.002	0
Al2O3	0.101	0.000202	0	-0.101
C	0.2	0.0004	0	-0.2
S		0	0	0
Ca(OH)2		0	0.013	0.013
MgO		0	0.856	0.856
NaAlO2		0	0.16	0.16
FeS		0	0.122	0.122
CaO		0	0.234	0.234
MnS		0	3.64	3.64
CaS		0	1.232	1.232
FeO		0	0.2	0.2
MnO		0	1.93	1.93
MgCO3		0	0	0
TOTAL	499.904	1	499.927	0.023

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Table C-4 : Smelt Formation at 800°C (Al Content 10X)

SPECIES	Smelt In	Smelt In	Smelt Out	Smelt Out-In
Run 057	g.	wt.fr.	g.	g.
	0	0		
H2O	352.3	0.704584	353.38	1.08
NaHCO3	0	0	0.217	0.217
Na2S	117.3	0.234595	114.66	-2.64
Na2SO3	0	0	0.08	0.08
Na2SO4	9.746	0.019492	8.87	-0.876
NaCl	9.75	0.0195	9.75	0
NaOH	0	0	1.543	1.543
CaCO3	6.5	0.013	5.77	-0.73
Fe2O3	0.347	0.000694	0	-0.347
Mg(OH)2	1.257	0.002514	0.046	-1.211
MnO2	0.602	0.001204	0	-0.602
SiO2	1.006	0.002012	1.005	-0.001
Al2O3	1.001	0.002002	0.16	-0.841
C	0.202	0.000404	0.135	-0.067
S		0	0.591	0.591
Ca(OH)2		0	0.014	0.014
MgO		0	0.813	0.813
NaAlO2		0	1.35	1.35
FeS		0	0.17	0.17
FeS2		0	0.268	0.268
MnS		0	0.584	0.584
CaS		0	0.499	0.499
FeO		0	0.013	0.013
MnO		0	0.015	0.015
MgCO3		0	0.03	0.03
TOTAL	500.011	1	499.963	-0.048

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DUES-FUNDED PROJECT SUMMARY

Project Title:	VOC in Kraft Mills
Project Code:	
Project Number:	F01708
PAC:	Recovery
Division:	Chemical Recovery and Corrosion Division
Project Staff	
Faculty/Senior Staff:	Junyong Zhu
Staff:	Garry Heedick
FY 98-99 Budget:	$35,000
Allocated as Matching Funds:	$50,000
Time Allocation	
Faculty/Senior Staff:	Junyong Zhu: 25%
Support:	Garry Heedick: 40%
Supporting Research	
M.S. Students:	Jeremy Thomas
Ph.D. Students:	
External:	Dr. Xinsheng Chai (Associate Scientist supported by DOE and State of GA)
	Dr. Pi-Hsin Liu (Post Doctor supported by DOE)

RESEARCH LINE/ROADMAP: Environmental Performance: 5. Reduce emissions of the entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule criteria while maintaining global competitiveness.

PROJECT OBJECTIVE:

Develop a VOC database of concentrations and vapor-liquid phase equilibrium on various kraft mill streams.

PROJECT BACKGROUND:

The release of VOC into air is an environmental concern. Many VOCs are on the list of hazardous air pollutants (HAPs). The cluster role now requires to control VOCs in many kraft mill processes. The present study will provide database for the control of VOC as well as for computer models to predict VOC emissions in kraft mills.

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SUMMARY OF RESULTS:

- Developed understanding and quantified VOC formation in pulping
- Develop understanding and quantify VOC formation during the evaporation of black liquors.
- Completed the work of Henry's constant of methanol in black liquors.
- Conducted another full mill sampling in both air and streams.

GOALS FOR FY 1999-2000:

- Conduct mill sampling in the recovery area
- Conduct study on effect of wood species on methanol formation in pulping
- Conduct study on effect of wood species on methanol formation in evaporation and storage tanks
- Conduct methanol formation in a pilot scale evaporator

DELIVERABLES:

- A report on methanol formation in black liquor storage tank and evaporators
- A report on the effect of wood species on methanol formation in kraft mills

SCHEDULE:

- Mill sampling: months 1-3
- Report on VOC formation using different wood specie: month 3-6
- Report on effect of wood species on methanol formation in evaporation: month 6-9
- Report on pilot scale evaporator: month 9-12

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

Volatile Organic Compounds (VOCs) in Kraft Mills Streams -

Henry's Law Constant of Methanol in Pulping Spent Liquors

Project F01708

Report 5

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

J.Y. Zhu, P.H. Liu, and X.S. Chai

March, 1999

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Henry's Law Constant of Methanol in Pulping Spent Liquors

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EXECUTIVE SUMMARY

The release of volatile organic compounds in kraft mills has been an environmental concern. The vapor-liquid equilibrium (VLE) of VOCs in mill streams is an key factor that dictates VOC air emission. Unfortunately, the VLE behavior of VOCs in most kraft mill streams are different from that in a binary VOC-water solutions. Develop good understanding of VLE behavior of VOCs in various mill streams has significant importance in providing data base for computer model prediction of VOC air emission and design strippers for VOC removal.

Because methanol has been identified as the main VOC species in kraft mill stream, in this study, a direct headspace gas chromatographic method was used to study the methanol Henry's constant in pulping spent liquors collected from kraft pulp mills and laboratory batch pulping processes using various wood species. The total solids content of the pulping spent liquors were less than 25%. It was found that temperature and inorganic solids, mainly sodium salts, are the two parameters that significantly affected the methanol Henry's constants. A two-parameter (temperature and liquor total solids content) empirical model was developed based on the experimental data to predict methanol Henry's constants in pulping spent liquors.

Keywords: Methanol, VOC, Henry's Constant, Black Liquor, Vapor-liquid Equilibrium, Headspace, Gas Chromatographic.

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INTRODUCTION

Henry's law constant directly relates the partial vapor pressure and the infinite dilution activity coefficient of a dissolved species in a given aqueous solution. The partial vapor pressure of a volatile pollutant species can be used to predict the air emission of the pollutant in many industrial operation sites, rivers, etc. It also dictates the design of strippers and other facilities to separate the volatile species. Therefore, the study of vapor-liquid equilibrium (VLE) of solute in infinite diluted solutions has significant practical importance in chemical engineering and environmental science.

We report on the Henry's law constants of methanol in pulping spent liquors in this study. It is well known that methanol can be formed in digesters through the reactions of methoxyl groups in hemicellulose and lignin of wood with hydroxide during pulp manufacturing processes in kraft pulp mills [1-3]. The formation of methanol during kraft pulping processes created an environmental concern, because methanol is soluble in water to become an important source of biodegradable organic compounds to increase the biochemical oxygen demand (BOD), furthermore, methanol is very volatile and can be released into atmosphere from various kraft mill operation processes. Methanol air emission in kraft mills is now regulated by the U.S. Environmental Protection Agency through the Cluster Rule [4]. The study on the Henry's law constant of methanol in various kraft mill streams provides a VLE database for emission predictions using computer simulation models [5, 6] to improve process operations and reduce methanol emission.

The infinite dilution activity coefficient of methanol in water has been reported in several studies [7-13], however, the data reported by these studies are not consistent; furthermore, limited understanding is available on whether or not these data are applicable to solution matrices that contains other than methanol and water, such as many solutions collected in pulp and paper process streams. It is not trivial and the objective of the present study to address the issue of inconsistency of the existing methanol activity coefficient data in diluted water solutions. The measurement methods used in these studies are certainly one factor contributed to the inconsistency. There are many experimental methods available for the study of infinite dilution activity coefficient as reviewed by Kojima et al. [14] recently. Most of these methods

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can be used to determine the Henry's constants of solute, but not without limitations in measurement accuracy and other related problems. Static headspace gas chromatography has been widely used to obtain VLE partitioning coefficients (or Henry's constants) for its accuracy, consistency, speed, and versatility. Direct [15, 16], indirect [17-19], and multiple extraction [20] headspace GC methods have been developed for this purpose. Headspace GC methods have been proven by numerous studies as an effective technique to determine dilution activity coefficient or Henry's law constants [15-21]. Gupta [21] indicated that the partial molar excess enthalpy derived from the infinite dilution activity coefficient of methanol and ethanol measured using a headspace GC method [18] is mostly closed to those measured by calorimetric values. In this study, a direct headspace gas chromatographic method described by Kolb et al. [16] is employed to directly determine the Henry's law constant of methanol in diluted solutions. The measurements in pulping spent liquors were used to derive an empirical correlation of methanol Henry's law constant for methanol air emission predictions in kraft mills.

EXPERIMENTAL

Measurement Facility and Method

All the measurements were conducted using a commercial headspace gas chromatograph. The instrument consists of a headspace sampler (HP-7694, Hewlett-Packard, Palo Alto, CA) and a capillary gas chromatograph (HP-6890, Hewlett-Packard).

The Henry's law constant H_i of a species i is defined according to the following equation:

$$H_i = \lim_{x \to 0} \frac{y_i \cdot P}{x_i} \qquad (1)$$

where x_i and y_i are the mole fraction of the species i in the vapor and liquid phase, respectively. For a solution system under equilibrium in a static headspace, we can assume that the vapor phase follows the ideal gas law,

$$y_i \cdot P = P_i^v = C_{Gi} \cdot RT \qquad (2)$$

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where C_{Gi} is the solute mole concentration in the headspace (vapor phase) and R is the universal gas constant. For a binary or a multi-component solution system with all the solutes under infinite dilution, the quantities of the solutes are negligible compared to the solvent, we can approximate the mole fraction of solute i in the liquid phase as,

$$x_i \approx \frac{n_i}{n_j} = \frac{C_{Li}}{\rho_j / M_j} = C_{Li} \cdot v_j \tag{3}$$

where C_{Li} is the solute concentration in the liquid phase under phase equilibrium, ρ_j, M_j, and v_j are the density, molecular weight, and the molar volume of the solvent, respectively.

Substitute Eqns. (2) and (3) into Eqn. (1), we can relate the Henry's law constant of species i to its VLE partitioning coefficient $K_i = C_{Li}/C_{Gi}$ in a static headspace,

$$H_i = \frac{RT}{v_j K_i} = \frac{\rho RT}{M \cdot K_i} \tag{4}$$

A direct headspace GC method [16] was used in the present study to determine the VLE partitioning coefficient K_i. In this method, we first measure the initial (before vapor liquid equilibrium study) methanol concentration C_0 in a sample black liquor using an indirect headspace GC method [20, 21] (a standard addition procedure). We then measured the methanol concentration C_G in the static headspace in terms of GC recorded peak area A. Therefore, we have

$$K_i = \frac{C_{Li}}{C_{Gi}} = \frac{C_0 - \beta C_{Gi}}{f \cdot A_i} \tag{5}$$

where f is the GC response factor and $\beta = V_G/V_L$ is called the phase ratio. $\beta = 1$ (or V_L=10 mL) was used in this study. Therefore, if K_i is much greater than 1, i.e., $K_i > 10$, $C_{Gi} << C_{Li}$ ($< C_0$) can be ignored in Eqn. (5), we have

$$K_i \approx \frac{C_0}{f \cdot A_i} \tag{6}$$

We used a standard water-methanol mixture solution with known methanol concentration of C_{s0} = 800 mg/L and methanol VLE partitioning coefficient K_{si}, e.g., K_{si} = 570 at 70°C [18], to calibrate f, we have

$$K_i = \frac{A_{si}}{A_i} \cdot \frac{C_o}{C_{so}} \cdot K_{si} \qquad (7)$$

where, A_{si} is the GC peak area recorded in measuring the headspace vapor of the standard solution at the temperature corresponding to K_{si}.

Pulping Spent Liquor and Chemicals

Pulping spent liquor also called black liquor from its color is an aqueous water solution containing dissolved organic and inorganic solids. It is a by-product of the wood deligninfication process in pulp and paper manufacturing. The dissolved organic materials are a complex substance derived from cellulose, hemicellulose, lignin, and other extractives in the wood. The soluble inorganic solids are mainly sodium salts. The contents of potassium salts are minimal. The total solids content of pulping spent liquor or weak (unconcentrated) black liquor is around 5-20% with the organic to inorganic ratio around 0.45. Black liquor is caustic with a pH value around 13. It also contains many volatile organic compounds (VOVs) formed during pulping, such as methanol, methyl ethyl ketone (MEK), dimethylsulfide (DMS), etc. The concentrations of these VOCs are very low and can be assumed within the limit of infinite dilution from a thermodynamic point of view.

Weak black liquors derived from various wood species collected from both several kraft pulp mills and laboratory pulping processes are used in this study. The total dissolved solids contents of the black liquors were less than 25%, therefore, the liquors can be considered aqueous solutions. Analytical grade of sulfonated lignin, sodium carbonate, sodium sulfate, and sodium chrolide, sodium hydroxide, dimethylsulfide (DMS), dimethyldisulfide (DMDS), methyl ethyl ketone (MEK), α-pinine, are also used to add into standard water-methanol solutions to study the effects these minor species contained in black liquors on the methanol Henry's constant in black liquors.

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Experimental Conditions

GC conditions: HP-5 capillary column at 30°C; carrier gas helium flow: 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions: gentle shaking for equilibration of the sample of 25 minutes, vial pressurization time of 0.2 min, sample loop fill time of 1.0 min., and loop equilibration time of 0.05 min.

RESULTS AND DISCUSSIONS

Equilibrium Time

One key factor in VLE study is to achieve vapor-liquid equilibrium. The commercial HP-7694 headspace sampler can apply gentle and strong shaking to the sample vial to accelerate the equilibrium process between the liquid and vapor phases. Sample volume used in the vial is one factor that affects the time required to achieve equilibrium. In the experiments, we used a phase ratio of $\beta = 1$, or a liquid sample volume $V_L = 10$ mL, and gentle shaking. We found that an equilibrium time of 25 minutes is sufficient to achieve methanol vapor-liquid equilibrium in the sample vial static headspace [22].

Measurement Uncertainty

Although black liquor can be treated as aqueous solution, the distribution of various dissolved solids in the liquor could be inhomogeneous, which makes it difficult to obtain uniform and representative samples during experiments. Therefore liquor sampling can contribute to the measurement uncertainty. Because Henry's law constant is derived from two separate measurements (the liquid phase and the vapor phase) in the present study, which also can contribute to the measurement uncertainty. We conducted 11 replica measurements of methanol Henry's law constant in a black liquor collected from a kraft mill to estimate the actual measurement uncertainty of this study. We found that the maximum error for single measurement is about 15%. However, the relative standard deviation was 8.8%. We conducted triplicate experiments and averaged the measurements; therefore, the actual measurement uncertainty of the data presented in this study is less than 8.8%.

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Effect of Temperature

From basic thermodynamics, the VLE partitioning behavior of any solute is strongly dependent on temperature. The operating process temperature of weak black liquor in kraft mills varies significantly. We measured the Henry's constants of 13 black liquors from both kraft mills and our laboratory pulping processes using birch and southern pine in a temperature range of 50-80°C. Our measurement results indicate that the Henry's constant of methanol in all the black liquors examined increases exponentially with temperature. We found that the logarithm of Henry's constant of methanol in all the black liquors fits to a line with the inverse of temperature in degree Kelvin very well. Table I lists the linear regression results along with the correlation coefficients for all the liquors tested. Only the results from 4 black liquor samples are shown in Fig. 1 for clarity. The linear relationship in Eqn. (8) agrees with the van't Hoff Equation in basic thermodynamic theory for solutes, i.e., the Henry's constant is proportional to the partial molar excess enthalpy, which is a function of temperature.

$$\ln(H) = \frac{a}{T} + b \qquad (8)$$

For comparative purposes, we also plotted the Henry's constants of methanol in a water mixture in Fig. 1. The results as listed in Table I show that the slopes of the data of all of the 13 black liquor samples were very close to the slope of the methanol-water mixture data. The relative standard deviations of the slopes of the data with (14 data sets) and without water (13 data sets) were only 5.8 and 5.0%, respectively. It is further noted that all the slopes from the black liquor data were slightly smaller than that of water-methanol mixture as shown in Table I, indicating that the methanol partial molar excess enthalpy in black liquor (a multi-component system) was only slightly smaller than that in a water solution (a two-component system).

Fig. 1 indicates that there are significant variations in measured methanol Henry's constant among various black liquors. The variations in the compositions of the black liquors such as the inorganic and organic solids contents, pH, and other species could contribute to the differences in the Henry's constants.

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Effect of Lignin Content

Black liquor contains significant amount of dissolved organic materials, such as wood lignin. To understand the effect of lignin on methanol Henry's constant in black liquor, we measured methanol Henry's constant in water-methanol solutions with the addition of sulfonated lignin. We found that the methanol Henry's constant is not effected by sulfonated lignin. Fig. 2 shows the normalized Henry's constants of methanol measured in water solutions at two temperatures, 70 and 80°C, with various sulfonated lignin concentrations.

Effect of pH

We took a similar approach to study the effect of pH on the Henry's constant of methanol in black liquors. Black liquor is a caustic solution with a nominal pH value around 13. Different amounts of sodium hydroxide were added into several methanol-water solutions. Measurements show that the methanol Henry's constant is proportional to the power of 0.2 of the hydroxide concentration as shown in Fig. 3. Considering that the variation of pH in black liquors is from 12-14, it can be concluded that the effect of pH on the methanol Henry's constant is not significant. It should be noted that the sodium ion concentration also contributes to the variations shown in Fig. 3. The effect of ionic strength, or more specifically, sodium salt concentration on methanol Henry's constant is discussed in the next section.

Effect of Inorganic Salt Concentration

The inorganic solids content in black liquors are significant. These inorganic solids are mainly sodium carbonate Na_2CO_3 and sodium sulfate Na_2SO_4 plus some minimal amounts of sodium thiosulfate $Na_2S_2O_3$, sodium chloride NaCl, and potassium salts. To understand the effect of inorganic solids on methanol Henry's constant, we measured the Henry's constant in water-methanol solution with the addition of Na_2CO_3 , Na_2SO_4 , $Na_2S_2O_3$, and NaCl. We found that the methanol Henry's constant increases linearly with the sodium salt mass concentration at a given temperature and the Henry's constants are not affected by the type of salt spiked as shown in Fig. 4. To illustrate the effect of various sodium salts on methanol Henry's constant in black liquors, we also plot the measured methanol Henry's constants in black liquors in Fig. 4. The total mass concentrations of the inorganic materials (more than 95% are sodium salts) in the 13 black liquor samples studied were obtained by subtracting the lignin (organic solids) contents

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from the measured total solids contents. The results show that the methanol Henry's constants in black liquors are only a linear function of the total salt mass concentration even though black liquor contains significant amounts of both sodium carbonate and sodium sulfate. We can use the following equation to express the effect of sodium salts on methanol Henry's constants in black liquors,

$$H = c \cdot S_{Salt} + d, \tag{9}$$

where S_{salt} is the total sodium salt mass concentration in the liquor.

Effects of DMS, DMDS, MEK, α-pinene

Many other chemical species, such as dimethylsulfide, dimethyladisulfide, MEK, α-pinene, contained in weak black liquors can affect the methanol Henry's constant through molecular interactions. To determine whether or not these compounds have significant effects methanol Henry's constants in black, we used methanol-water solutions with the addition of these compounds separately to study the their individual effects on methanol Henry's constant. The results indicate that the effects of these compounds at the concentration levels present in weak black liquor on methanol Henry's constant is significant as shown in Figs. 5-8.

Empirical Correlation

From above discussion, we found that temperature and inorganic solids content are the two main parameters that affect methanol Henry's constant in black liquors. Because the concentration variations of most of the minor species contained in black liquors, such as pH, lignin concentration, and other organic compounds, are not significant, we can conclude that the effects of minor species on methanol Henry's constants will not important. In black liquors, the ratio of the inorganic to organic solids does not vary significantly. Because, the determination of total solids content is much easy with very good accuracy. Therefore, we can use the total solids content S to account for the effect of inorganic sodium salts on methanol Henry's constant. To demonstrate the validity of this assumption, we plotted the measured methanol Henry's constants in the 13 black liquors against the total solids contents. As shown in Fig. 7, we found the methanol Henry's constant is linearly proportional to total solids content at four different temperatures tested. The data scattering can be attributed to the actual variations in methanol

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Henry's constants due to the effects from minor parameters, such as pH, other components, and the small variations of inorganic/organic ratio from liquor to liquor. This is demonstrated by the fact that the methanol Henry's constants measured in a given black liquor sample at the 4 temperatures (50, 60, 70, and 80°C) are very consistent, i.e., all the measured data points either lower or higher than the expected (regression predicted) value. As always, experimental errors always contributed to the data scattering.

We developed a simplified empirical model based our experimental data as follows:

$$H = m\exp(-\frac{A}{T}) + B \cdot S + C. \qquad (10)$$

where C represents the total contributions from all the possible parameters other than temperature and total solids contents.

We then conducted a nonlinear least squares curve fit using the performance measure of $\varepsilon = \sum_i (H_i - H_{\text{pred},i})^2$. We found that $m = 11.96\text{X}10^9$, $A = 5978$, $B = 4.94$, and $C = 30.0$, respectively, with H in Pa. A negative value of C parameter indicate that the combined effects of the other parameters not included in the correlation (10) reduced the methanol Henry's constant in weak black liquors. For example, dimethylsulfide present in weak black liquor reduced the methanol Henry's constant as shown in Fig 6. To demonstrate the goodness of fit of the proposed empirical model, Fig. 8 plot the direct comparison of the methanol Henry's constants of 13 black liquors measured at 4 temperatures with those predicted using Eqn. (10). We found that the most of the data points are within 15% error margin, indicating that the model can successfully predict the methanol Henry's constants in different black liquors.

CONCLUSIONS

We measured methanol Henry's constants in various kraft pulping spent liquors collected from kraft mills and laboratory pulping processes using a headspace gas chromatographic technique. We found that temperature and inorganic solids content are the two major parameters that affect methanol Henry's constants. The effects from other parameters, such as pH, lignin content, and other organic compounds are insignificant. We developed a two parameter

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(temperature and total solids content) empirical model for the prediction of methanol Henry's constant based on the experimental data obtained in this study. The model prediction correlates with experimental data very well.

ACKNOWLEDGEMENT

This research was supported by the U.S. Department of Energy (Grant DE-FC07-96ID13438).

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Fig. 1

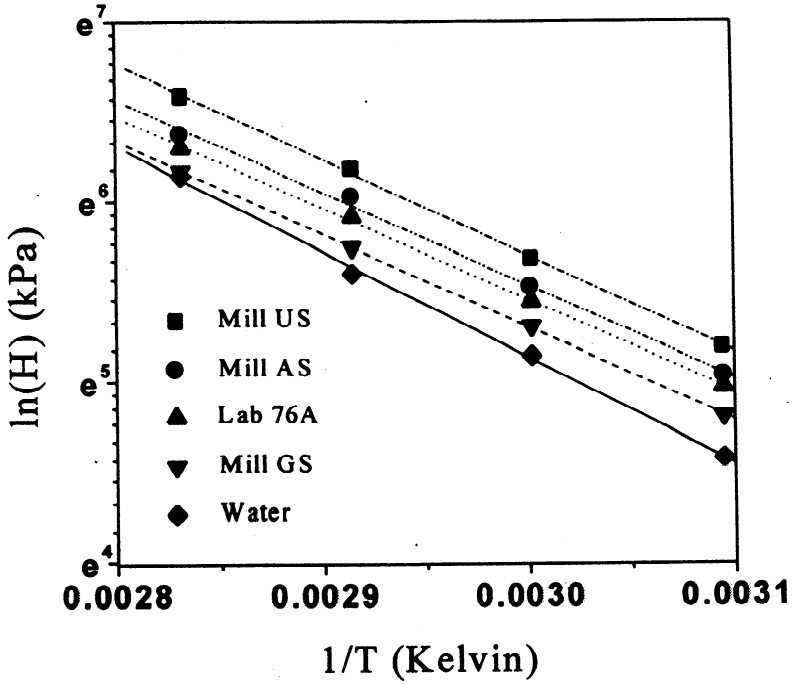

Fig. 2

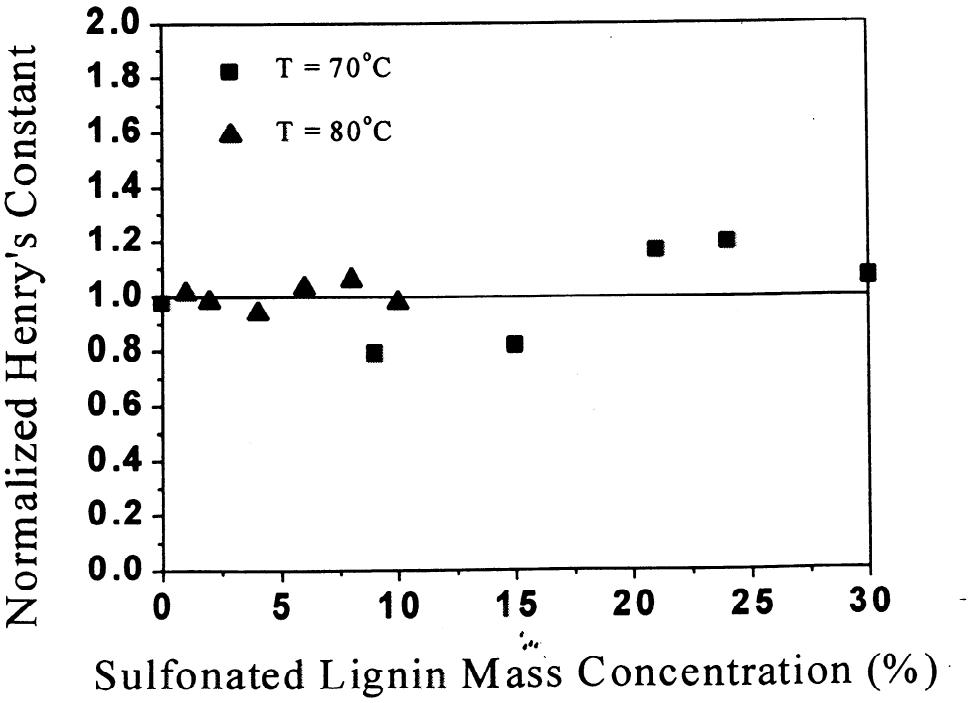

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Fig. 3

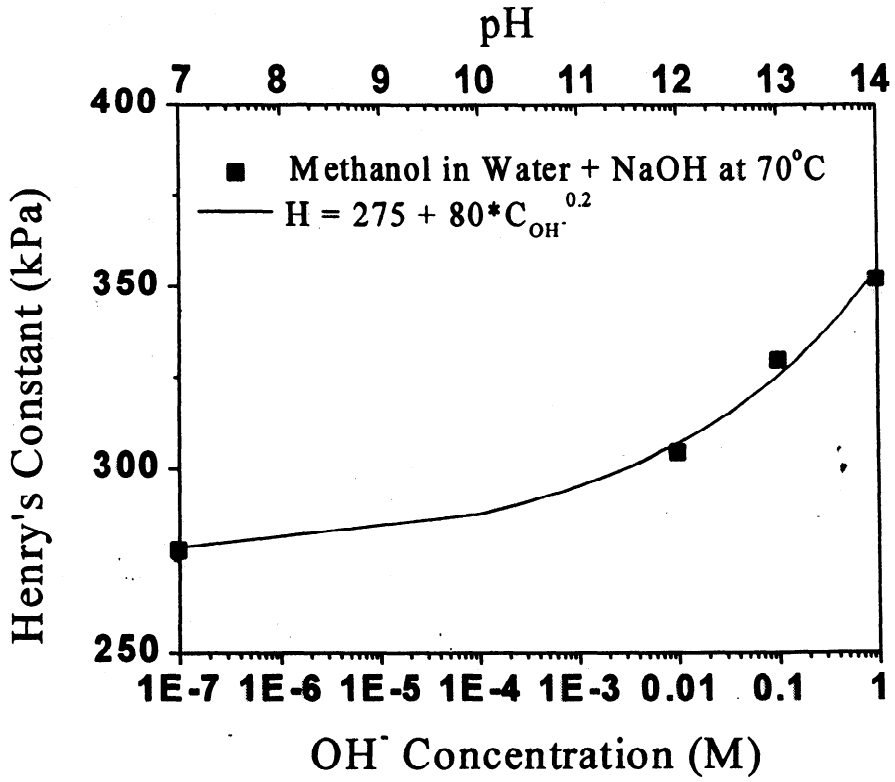

Fig. 4

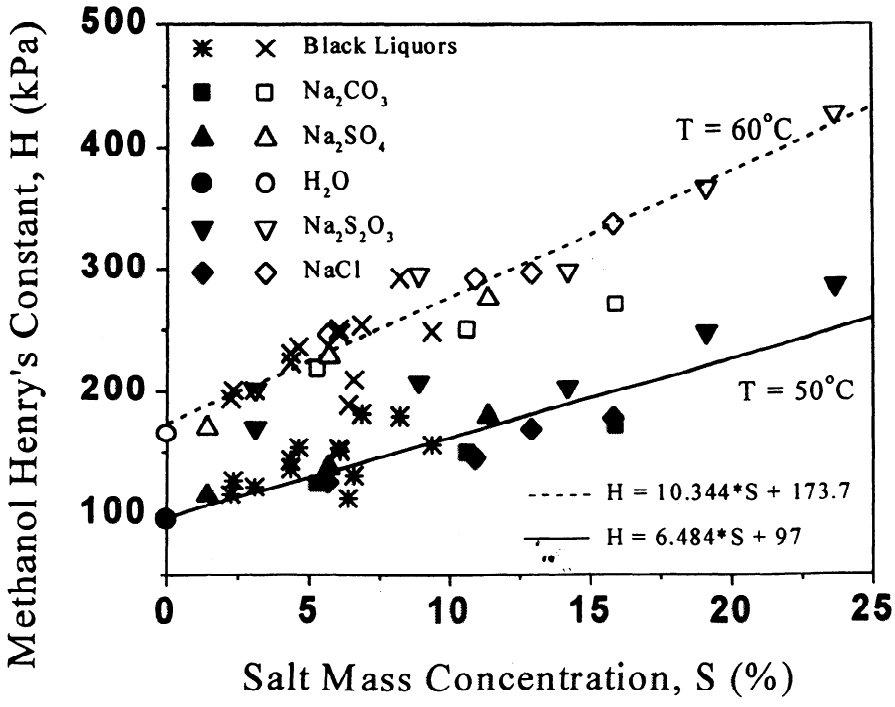

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Fig. 5

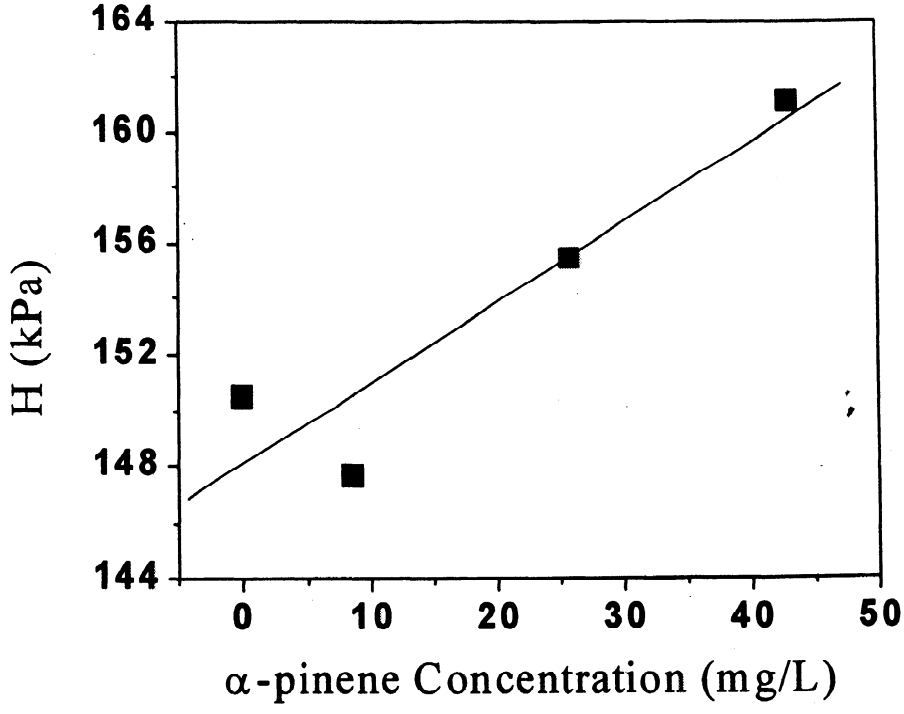

Fig. 6

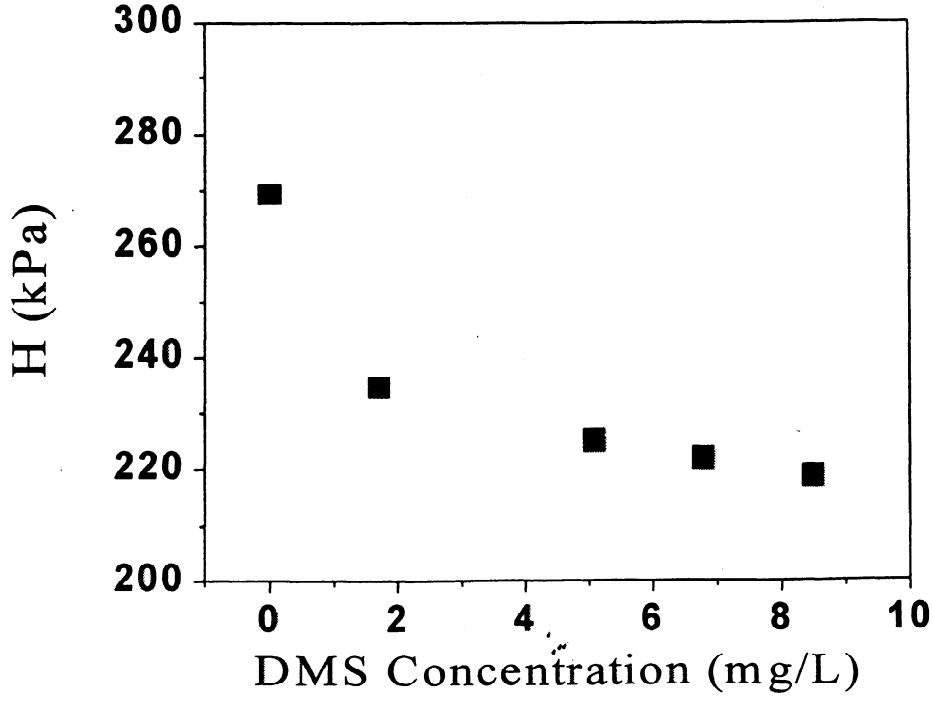

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Fig. 7

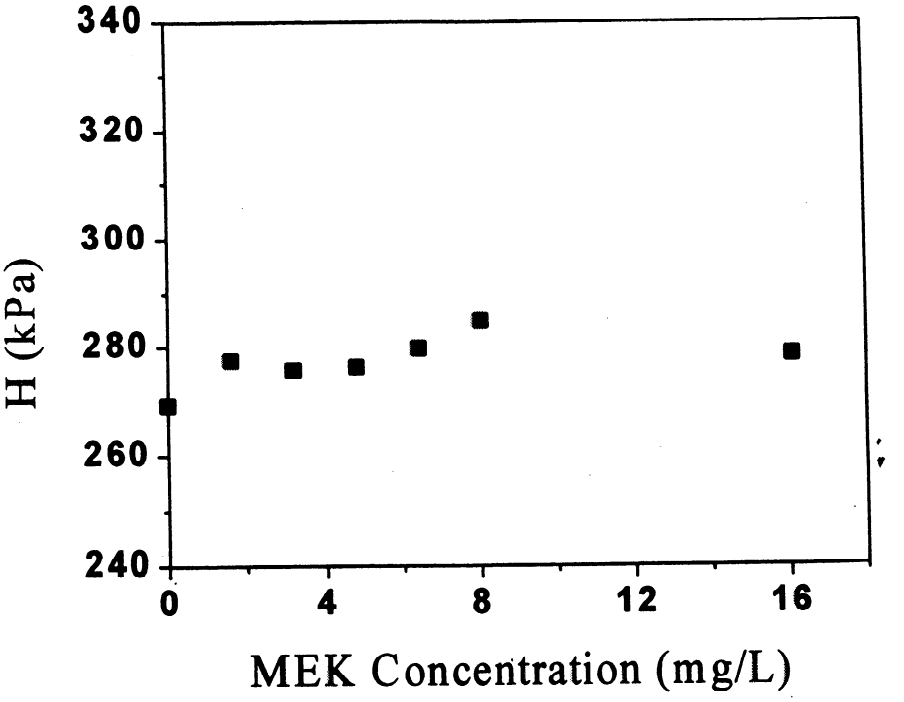

Fig. 8

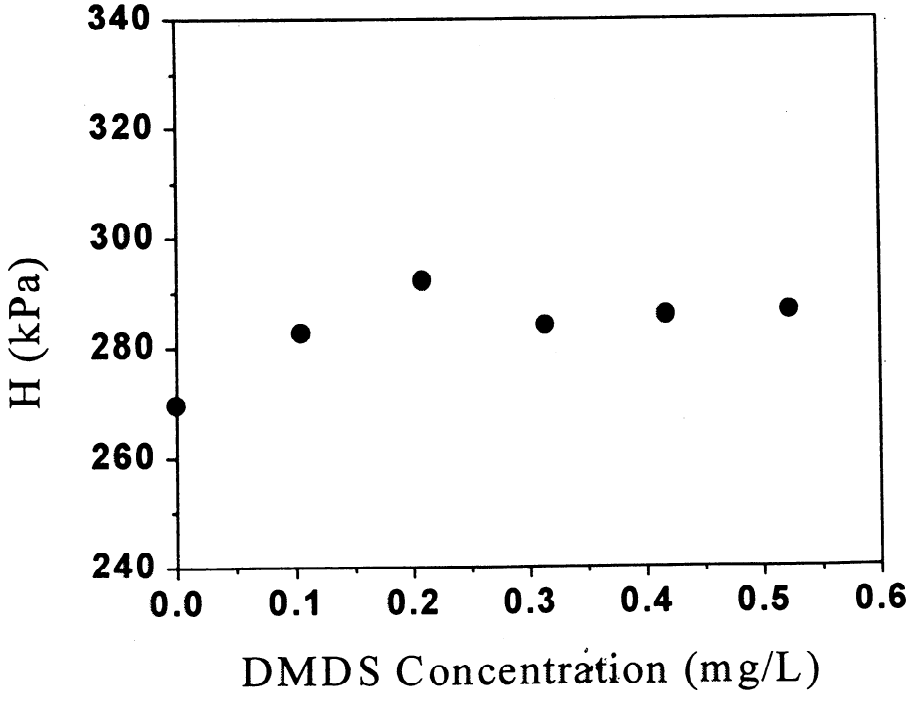

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Fig. 9

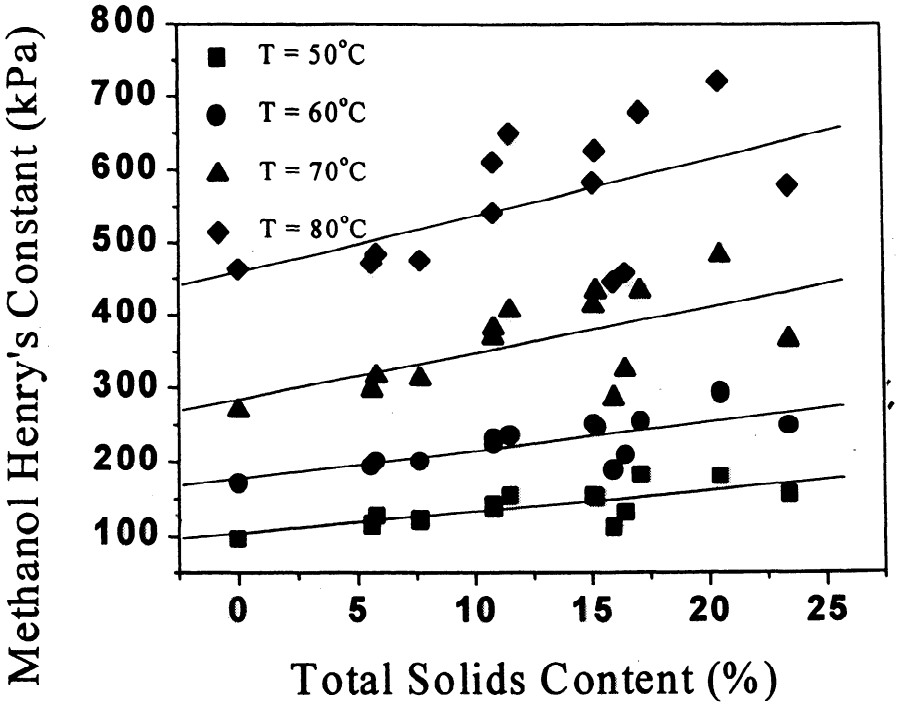

Fig. 10

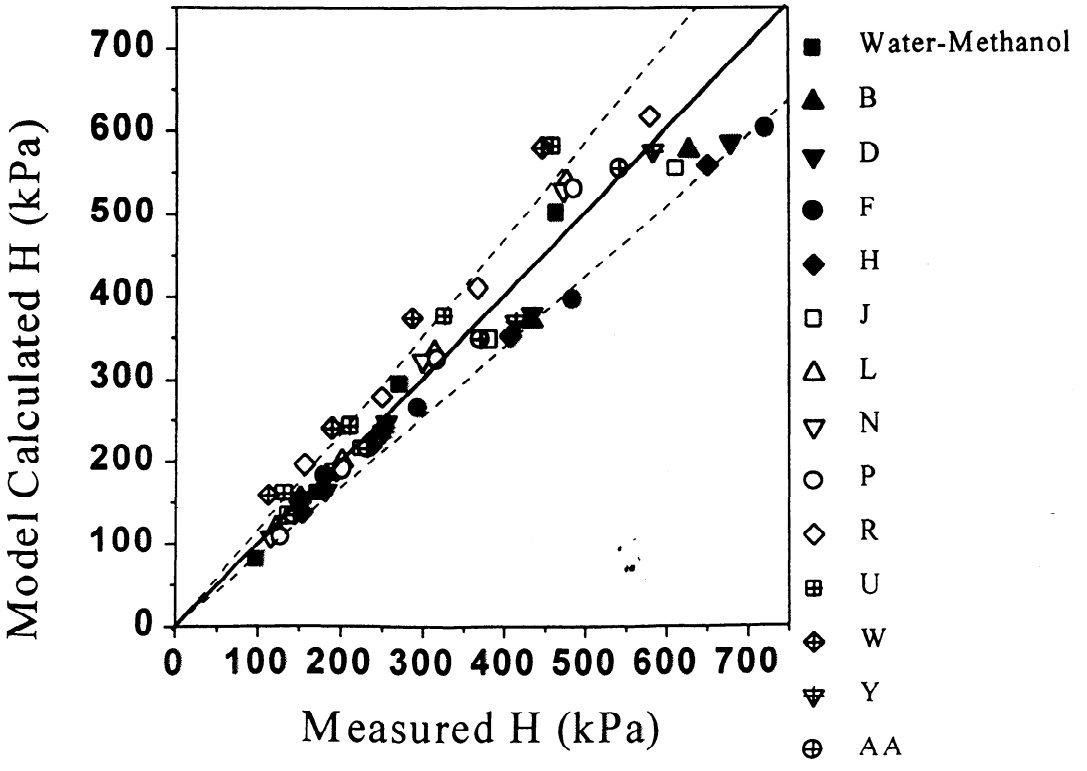

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Table I A list of fitting parameters of Eqn. (8) for a water-methanol mixture and black liquors.

Sample	a	b	Correlation Coefficient
Water-Methanol	-5878	22.766	0.9992
B	-5337	21.708	0.9996
D	-5164	21.024	0.9981
F	-5092	20.729	0.9996
H	-5179	20.835	0.9999
J	-5525	22.118	0.9980
L	-5119	20.988	0.9947
N	-5553	22.187	0.9983
P	-5734	22.648	0.9996
R	-5325	21.233	0.9997
U	-5101	20.623	0.9999
W	-4930	20.305	0.9991
Y	-4793	19.723	0.9991
AA	-5120	20.857	0.9996
Mean	**-5275**	**N/A**	**0.9989**
RSTD	**5.8%**	**N/A**	**0.14%**

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

Volatile Organic Compounds (VOCs) in Kraft Mills Streams -

The Formation of Volatile Organic Compounds (VOCs) During Pulping

Project F01708

Report 4

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

J.Y. Zhu, X.S. Chai, and B. Dhasmana

November, 1998

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The Formation of Volatile Organic Compounds (VOCs) During Pulping

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EXECUTIVE SUMMARY

The emission of volatile organic compounds (VOCs) in pulp and paper mills has been an environmental concern. VOCs were mainly formed in the pulping process in kraft mills. These VOCs are soluble in water and become an important source of biodegradable organic compounds to increase the biochemical oxygen demand (BOD). Furthermore, these species can also be released into the atmosphere at the process temperatures of kraft mill streams. The quantity of VOC formed (VOC yield) during pulping was not reported in the literature. Therefore, research on VOC yield during various pulping conditions using different raw materials can provide useful information to estimate VOC formation in pulp mills.

This study measured the time-dependent concentration profiles of major water-soluble volatile organic compounds (VOCs), i.e., methanol, acetone, and methyl ethyl ketone (MEK), during conventional pulping processes of southern pine, birch, and kenaf in a laboratory digester. These VOC species were mainly formed in the early stages of the cooking. The study shows that more methanol is formed in kraft pulping than in soda pulping. The study also verifies the conclusion found in the literature that hardwood pulping produces more methanol than softwood. Kinetic analysis indicates that the overall methanol formation reaction follows Arrhenius kinetics well. The catalyst, anthraquinone, increased the methanol formation in softwood kraft pulping, but reduced methanol formation in kraft hardwood pulping.

From the data obtained, this study also developed an empirical methanol formation model in conventional laboratory pulping that can be used for mill methanol formation estimations. Initial mass balance was obtained using the model developed. Future study is needed to obtain lignin demethylation kinetics for better prediction of methanol formation using the developed model.

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INTRODUCTION

The formation of volatile organic compounds (VOCs), such as methanol and methyl ethyl ketone (MEK), during kraft pulping processes has been an environmental concern. These VOCs are soluble in water and become an important source of biodegradable organic compounds to increase the biochemical oxygen demand (BOD). Furthermore, these species can also be released into the atmosphere at the process temperatures of kraft mill streams. With the increasingly restrictive environmental regulations such as the Cluster Rule [1] by the U.S. Environmental Protection Agency, many VOCs are now on the list of hazardous air pollutants (HAPs) that are required to be controlled. The knowledge of VOC formation during the pulping process is limited. The quantity of VOC formed (VOC yield) during pulping was not reported in the literature. The effects of pulping conditions and catalyst on the VOC yield during pulping have not been studied. Therefore, research on VOC yield during various pulping conditions using different raw materials can provide useful information to estimate the VOC formation in pulp mills. The knowledge gained can help to develop technologies to reduce VOC emission at its source, i.e., during pulping.

Methanol has been identified as the main alcohol in pulp mill process streams [2-4]. A list of various VOCs present in pulp mill streams was summarized by Bethge and Ehrenborg [5] and Blackwell et al. [6]. According to Clayton [7], methanol could be formed by the rapid alkaline hydrolysis reaction of 4-O-methylglucuronic acid residues in hemicellulose (or hydrolyzation of xylan). Although methanol can also be formed through the demethylation of methoxyl groups in lignin [6, 8], the amount of methoxyl groups that can be demethylated is very small [8]. Therefore, it is reasonable to assume that the majority of methanol is formed through the hydrolyzation of xylan [7, 8]. Wilson and Hrutfiord [2] conducted a study on the reaction mechanism of VOCs using mill samples and analytical grade chemicals. They proposed that fermentation is the main formation pathway to all alcohol except methanol, and methyl ketones are formed by air oxidation of wood extractives followed by a reverse alcohol condensation. Later, Wilson et al. [9] studied the effect of wood species on the formation of VOCs in pulping and concluded that hardwood can yield many more VOCs than softwood.

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The objective of the present study is to quantify VOC yields from different pulping processes using various raw materials. The concentrations of methanol, acetone, and methyl ethyl ketone (MEK) during each cooking process were obtained by analyzing the cooking liquor samples collected during various stages of pulping. The information obtained can be used to develop VOC formation model for the prediction of VOCs released in pulp mills.

EXPERIMENTAL

The pulping experiments were carried out in a laboratory batch digester (ME&K). Conventional pulping processes were employed in this study. The load of each batch cooking was 800 grams of oven-dried (O.D.) chips. Four types of raw materials were used in this study, i.e., southern pine (softwood), birch (hardwood), and kenaf bast and kenaf core (nonwood). Southern pine and birch were pulped separately by both kraft and soda processes, with and without a catalyst, anthraquinone (AQ). Kenaf bast and core were pulped separately using soda-AQ process only. The detailed pulping conditions are listed in Table I. After the addition of the chips and cooking liquor, the temperature of the digester was raised from room temperature to 100°C in 20 minutes. Then it was brought to 170°C in an hour, and maintained at 170°C for two hours. After the completion of the cooking, the digester was cooled to room temperature by draining the black liquor. The pulp was thoroughly washed before the handsheets were made for kappa number and viscosity analysis. The final kappa numbers of fibers from all the cooking processes are listed in Table II.

During each cooking process, a small amount (15 mL) of cooking liquor was collected at about 15-20-minute intervals after the temperature reached 100°C. The concentrations of methanol, acetone, and methyl ethyl ketone (MEK) in the collected liquors were analyzed using an indirect headspace gas chromatographic method that we developed [4]. We also determined the absorption of dissolved lignin in cooking liquor by UV spectrophotometry [10].

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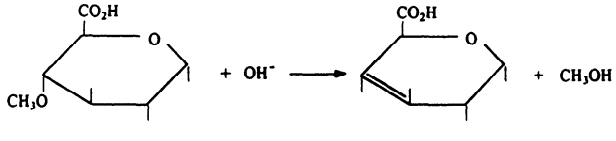
RESULTS AND DISCUSSIONS

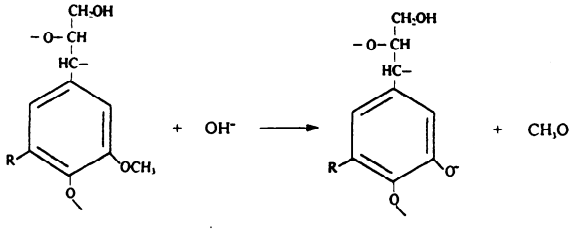
The VOCs in the kraft mill condensate streams, especially those most quoted in the literature [5, 6], include alcohols, ketones, phenolics, terpenes, and organic sulfur compounds. The composition of VOCs formed during pulping is related to the wood species and the pulping process employed. For example, a very significant amount of α-pinene was formed during softwood cooking. For kraft pulping, it was found that dimethyl sulfide is a dominant malodorous organic compound remaining in the cooking liquors [4]. The amount of methyl mercaptan (MM) is not significant in the solution because of its low boiling point. Methanol, acetone, and MEK were the major water-soluble volatile organic compounds found in the cooking liquors from both kraft and soda pulping process. In this study we found that methanol concentration in the cooking liquors could reach 1000 mg/L. The amounts of acetone and MEK were relatively low compared to methanol, about 2 to 8 mg/L in the cooking liquors. The other water-soluble volatile compounds, such as ethanol, were not significant in the black liquors.

Methanol Mass Balance and Formation Model

The purpose of chemical pulping is to separate fibers that consist of cellulose and hemicellulose by dissolving wood lignin in the cooking liquor through the so-called delignification process. During a pulping process, methanol can be formed mainly through the degradation of 4-O-methyl-D-glucuronoxylans in hemicellulose through hydrolysis [7] as shown in reaction (1a). According to Sarkanen et al. [8], methanol formation through the demethylation of the aromatic methoxyl groups in lignin structure, as shown in reaction (1b), is insignificant.



(1a)



(1b)

In this study, we measured the methanol concentrations in the cooking liquors collected at various stages of all the pulping experiments. Fig. 1 shows the methanol concentration and UV absorption of the dissolved lignin measured as a function of cooking time in a kraft cooking of southern pine (softwood). The results show that the methanol concentration increased as temperature increased. It was found that the formation of methanol increased along with dissolved lignin during the first 1.5 hours of the pulping process. After that, the dissolved lignin concentration continued to increase, while the methanol content leveled off. Reaction (1a) was supported by xylan hydrolysis studies using model xylan compounds [7]. The methoxyl groups from the 4-O-methyl-glucuronoxylan was found close to zero after 2 hours of hydrolysis reactions [7]. We can carry out a mass balance calculation to estimate the methanol yield based on the assumptions of 100% hydrolysis of methoxyl groups in xylan. The amount of 4-O-methyl-glucuronic acid $m_{me\text{-}glu\text{-}acid}$ in a wood can be expressed as the xylan content x_{xylan} times the ratio of 4-O-methyl-glucuronic acid to xylose $R_{me\text{-}glu\text{-}acid}$,

$$m_{me-glu-acid} = x_{xylan} \cdot R_{me-glu-acid} \cdot m_{wood} \tag{2}$$

According to reaction (1a), 1 M of 4-O-methyl-glucuronic acid forms 1 M of methanol. Therefore the amount of methanol formed would be:

$$m_{MeOH\text{-}xylan} = \frac{M_{MeOH}}{M_{me-glu-acid}} \cdot m_{me-glu-acid} \cdot f\,, \tag{3}$$

where $M_{MeOH} = 31$ and $M_{me\text{-}glu\text{-}acid} = 186$ are the molecular weight of methanol and the 4-O-methyl-glucuronic acid in wood xylan, respectively. f is the fraction of the 4-O-methyl-glucuronic acid hydrolyzed and is assumed to be equal to 1 in this study. The methanol concentration (mg/L) in cooking liquor can be expressed as

$$\left[C_{MeOH-xylan}\right] = \frac{m_{MeOH-xylan}}{R_{LW} \cdot m_{wood}} \times 10^6 = \frac{M_{MeOH}}{M_{me-glu-acid}} \cdot \frac{f \cdot x_{xylan} \cdot R_{me-glu-acid}}{R_{LW}} \times 10^6\,, \tag{4}$$

where R_{LW} is the liquor-to-wood mass ratio and the density of the cooking liquor is assumed equal to 1 kg/L, same as water.

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Table III lists the sample calculations of methanol concentration using Eqn. (4) for the southern pine (softwood) and white birch (hardwood). The xylan content x_{xylan} and the ratio of the 4-O-methyl-glucuronic acid to xylose $R_{me\text{-}glu\text{-}acid}$ listed in the Table are based on the data given by Biermann [11] and Fengel and Wegener [12], respectively. The calculated concentrations of methanol formed from hemicellulose degradation through hydrolysis reactions in the cooking liquors of southern pine and birch are 937 and 781 mg/L, respectively. The table also lists the experimentally measured methanol concentrations (averaged over kraft, kraft-AQ, and soda-AQ processes) in the final cooking liquors in this study. The calculated methanol concentrations account for 70% and 77% of those measured in birch and pine liquors, respectively. The unaccounted methanol must be formed by the demethylation of methoxyl groups in lignin.

Similar to the derivation of methanol formation from 4-O-methyl-glucuronic acid in xylan, we can derive a mathematical model to predict methanol formation from lignin based on reaction (1b). As shown in Eqn. (5), the model takes the following facts into consideration: (1) softwoods contain only coniferyl alcohol, while hardwoods contain both coniferyl (50-75%) and sinapyl alcohols (25-50%) [11]; (2) sinapyl alcohol contains two methoxyl groups while the coniferyl alcohol only has one, as shown in Fig. 2; and (3) the reaction rates of the first and the second methoxyl groups of sinapyl lignin are different.

$$m_{MeOH-lignin} = M_{MeOH}\left(q_c \frac{m_{lig-Conf}}{M_{lig-Conf}} + (q_{s1}+q_{s2})\frac{m_{lig-Sinp}}{M_{lig-Sinp}}\right)$$

$$= M_{MeOH}\left(\frac{q_c \cdot R_{Conf-alcoh}}{M_{lig-Conf}} + \frac{(q_{s1}+q_{s2})\cdot R_{Sinp-alcoh}}{M_{lig-Sinp}}\right) x_{lignin} \cdot m_{wood}, \qquad (5)$$

where $M_{lig\text{-}Conf} = 177$ and $M_{lig\text{-}Sinp} = 198$ are the molecular weights of lignin for coniferyl and sinapyl alcohols, respectively; q_c, q_{s1}, and q_{s2} are the fractions of coniferyl methoxyl groups, the first and second methoxyl groups of sinapyl lignin demethylated, correspondingly; and x_{lignin} is the lignin content in the wood. The methanol concentration (mg/L) in a cooking liquor contributed by lignin demethylation can be expressed as

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$$\left[C_{MeOH-lignin}\right] = \frac{m_{MeOH-lignin}}{R_{LW} \cdot m_{wood}} \times 10^6$$

$$= M_{MeOH}\left[\frac{q_c \cdot R_{Conf-alcoh}}{M_{lig-Conf}} + \frac{(q_{s1}+q_{s2}) \cdot R_{Sinp-alcoh}}{M_{lig-Sinp}}\right] \cdot \frac{x_{lignin} \times 10^6}{R_{LW}} \quad (6)$$

According to Sarkanen et al. [8] wood lignin demethylation reaction consists of a rapid phase followed by a slower phase. Sarkanen et al. [8] studied various wood lignin demethylation reactions at a temperature range of 170-200°C with alkali concentration of 5-15%. It is obvious that the reaction rates of the first and the second methoxyl groups in sinapyl alcohol lignin of hardwood are different. This difference is neglected (or $q_{s1} = q_{s2}$) for simplification in the present calculation because limited data are available in the literature about the reaction rates of sinapyl lignin methoxyl groups. Based on the experimental data of Sarkanen et al. [8], we assumed that the fractions of methoxyl groups in sinapyl lignin demethylated are about 2.7% (or $q_{s1} = q_{s2} = 0.027$) for estimation of methanol formation in pulping of birch (hardwood). Because softwood lignin demethylation data are not available and softwood (pine or coniferyl lignin) is usually more difficult to delignin (has a slow reaction rate) than hardwood (e.g., birch), 1.5% is arbitrarily assumed ($q_c = 0.015$) for estimation.

The calculated concentration of methanol formed from lignin demethylation in the cooking liquors using Eqn. (6) for southern pine and birch are 255 and 197 mg/L, respectively, as listed in Table IV. The lignin content x_{lignin} and the ratios of coniferyl and sinapyl alcohol to lignin $R_{Conf-alcoh}$ and $R_{Sinnf-alcoh}$, respectively, are from Biermann [11]. The calculation results shown in Table IV suggest that with the assumption of only 2.7% and 1.5% lignin demethylation (for birch and pine, respectively), lignin demethylation contributes to about 20% of the methanol formed in pulping. In other words, though lignin demethylation is insignificant as suggested by Sarkanen et al. [8], its contribution to methanol formation cannot be neglected.

By combining Eqs. (4) and (6), we can obtain an empirical mathematical model to estimate the methanol concentration in the final pulping spent liquor.

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$$[C_{MeOH}] = \frac{m_{MeOH} \times 10^6}{R_{LW} \cdot m_{wood}} = [C_{MeOH-xylan}] + [C_{MeOH-lignin}]$$

$$= \left[\frac{f \cdot R_{me-glu-acid}}{M_{me-glu-acid}} \cdot x_{xylan} + \left(\frac{q_c \cdot R_{Conf-alcoh}}{M_{lig-Conf}} + \frac{(q_{s1} + q_{s2}) \cdot R_{Sinp-alcoh}}{M_{lig-Sinp}} \right) \cdot x_{lignin} \right] \frac{M_{MeOH} \times 10^6}{R_{LW}} \quad (7)$$

Table V lists the methanol mass balance based on calculations using Eqns. (4), (6), and (7) and the experimentally measured data. We found that all of the methanol was accounted for except for about 10%. Considering the multiple estimation of the various parameters adopted from the literature and approximations taken to simplify the calculation, the model provided a very good empirical prediction.

Methanol Formation Reaction Rate

Since xylan hydrolysis contributes to about 75% of the methanol formed during pulping (with the assumption of 100% methoxyl group hydrolyzed), we can use the rate of xylan hydrolysis reaction (1a) to represent the overall methanol formation reaction rate for simplification as follows,

$$\frac{d[C_{MeOH}]}{dt} = -k[C_{CH_3O^+}] \cdot [C_{OH^-}]. \quad (8)$$

The methoxyl concentration is equal to its initial concentration minus the methanol concentration $[C_{MeOH}]$, i.e., $[C_{CH_3O^+}] = C^0_{CH_3O^+} - [C_{MeOH}]$. The hydroxide concentrations $[C_{OH^-}]$ in the cooking liquor was found to follow an exponential decay function, in agreement with those reported by Liaw and Krishnagopalan [13]. Eqn. (9) is a regression obtained hydroxide concentration profile for a kraft softwood pulping process shown in Fig. 1.

$$[C_{OH^-}] = 0.11 + 1.07 \exp\left(-\frac{t}{29.0}\right) = 0.11 + 1.07 \exp\left(-\frac{T-100}{24.86}\right) \quad (9)$$

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Fig. 1 also shows a typical methanol concentration profile at various stages of a kraft softwood pulping experiment we conducted. To obtain an analytical solution for k, we used a Boltzmann function (expressed in Eqn. (10)) to fit the measured methanol concentration.

$$[C_{MeOH}] = C_T + \frac{C_0 - C_T}{1 + \exp\left(\frac{t - t^*}{\Delta t}\right)}, \tag{10}$$

where C_T = 1000 mg/L and C_0 = 248 mg/L and are the final and the initial methanol concentrations, respectively, obtained from curve fitting for this particular experiment as shown in Fig. 1; and t^*=71.4 and Δt=11.4 are two time parameters of the Boltzmann distribution derived from regression. By taking the derivative vs. time of Eqn. (10), we have

$$\frac{d[C_{MeOH}]}{dt} = \frac{\exp\left(\frac{t - t^*}{\Delta t}\right)}{\left[1 + \exp\left(\frac{t - t^*}{\Delta t}\right)\right]^2} \cdot \frac{C_T - C_0}{\Delta t} = \frac{(C_T - [C_{MeOH}])([C_{MeOH}] - C_0)}{C_T - C_0} \cdot \frac{1}{\Delta t} \tag{11}$$

Combining Eqns. (8) and (11) with the assumption that $C^0_{CH_3O^-} = C_T$, we have

$$k = \frac{([C_{MeOH}] - C_0)}{(C_T - C_0) \cdot \Delta t} \cdot \frac{1}{[C_{OH^-}]} \tag{12}$$

Since both the methanol and hydroxide concentrations are directly related to the pulping temperature, we can find the methanol formation reaction rate k as a function of temperature for the data presented in Fig. 1. Furthermore, we also can express the reaction rate k in the Arrhenius form as shown in Eqn. (13),

$$k = Z \cdot \exp\left(-\frac{E_A}{RT}\right) = \frac{([C_{MeOH}] - C_0)}{(C_T - C_0) \cdot \Delta t} \cdot \frac{1}{0.11 + 1.07 \exp\left(-\frac{T - 100}{24.86}\right)} \tag{13}$$

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We conducted a linear regression analysis for the calculated reaction rate k in a temperature range of 100–170°C as shown in Fig. 3. We found that the natural logarithm of k vs. the inverse of temperature in Kelvin fits a straight line very well, suggesting that the reaction follows Arrhenius kinetics. From the regression results, we can obtain the reaction activation energy E_A = 1.2914x10^8 J/mol and the kinetic pre-exponential factor Z = 7.1528x10^{14}. We found that for all the pulping processes conducted in this study, the overall methanol formation reactions follow Arrhenius kinetics.

We would like to point out that the above analysis is an empirical analysis with the assumption that all the methanol is formed through hemicellulose hydrolysis and the hydrolysis reaction is homogeneous. Clearly, the diffusion of hydroxide in the cooking solution into a wood chip is an important factor in the actual heterogeneous pulping reactions. Furthermore, large errors may occur in this type of analysis due to limited measurements taken during the temperature ramping period of the pulping process as well as the sampling and measurement uncertainties. Therefore, quantitative comparisons of the activation energies of methanol formation reactions among various pulping processes are not very meaningful and were not conducted in this study. However, the above estimation can provide qualitative information about methanol formation during a pulping process.

Comparisons Between Softwood and Hardwood

Figures. 4 and 5 show the concentration profiles of VOCs during kraft and soda pulping of softwood and hardwood. We found that the methanol concentration profiles are almost identical for both except that more methanol is produced in hardwood cooking than in softwood cooking. More methanol formation was also reported by Wilson et al. [9]. Hardwood has a higher content of 4-O-methyl-D-glucuronoxylans in hemicellulose than softwood does, and hardwood lignin has more methoxyl groups than softwood lignin does [11]. Softwoods contain only coniferyl alcohol, while hardwoods contain both coniferyl (50-75%) and sinapyl alcohols (25-50%). Sinapyl alcohol contains more methoxyl groups than coniferyl alcohol as shown in Fig. 2. Furthermore, the peak methanol formation rate in hardwood pulping is higher than that in softwood pulping. Ninety percent of the methanol was formed within the first 75 minutes in the

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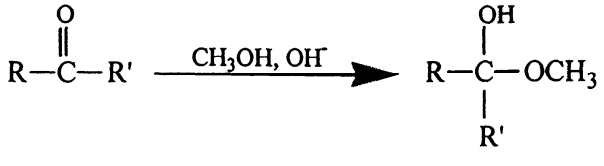
hardwood pulping processes. It took about 90 minutes to achieve 90% of the methanol in softwood pulping.

Figures. 4a and 5a also indicate that kraft pulping always yields more methanol than soda pulping does for both the hardwood and the softwood used in this study. As mentioned above, alkaline hydrolysis, as shown in reaction (1a), is the dominant methanol formation mechanism during most of a pulping process. In a kraft process, the presence of hydrogen sulfide ions can greatly facilitate delignification because of their superior nucleophilicity, as compared with hydroxyl ions. Therefore more hemicellulose and dissolved lignin are released from wood chips in the kraft pulping process. As a result, more methanol can be formed through the demethylation reactions of xylan and lignin.

According to Wilson and Hrutfiord [2], all of the ketones found in pulping, as methyl ketones, are formed through the air oxidation of extractives followed by decomposition of the extractive hydroperoxide, which undergoes a reverse alcohol condensation at a high temperature in the digester. We found in this study that the major ketone species generated in all the pulping processes were acetone and MEK. The concentration profiles of these ketones during the pulping were quite different from those of methanol as shown in Figs. 4b and 5b. In the cookings of the softwood, the profiles of acetone and MEK measured in the kraft pulping process are similar to those measured in the soda pulping, i.e., the concentrations of acetone and MEK reached a maximum at 50 minutes and then decreased after the cooking temperature reached 170°C. This behavior could be explained as a result of hemiacetals, or hemiketals, reactions between methanol and ketones [14]. Either acetals or ketals can react with methanol to form hemiacetals or hemiketals under certain conditions as follows:



Aldehyde or ketone — Hemiacetal or hemiketal (14)

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which leads to a decrease in ketone concentration as cooking continues. However, some other researchers believe that the equilibrium between acetal/ketal and the corresponding aldehyde/ketone is unaffected by hydroxide [15], which contradicts the above explanation. The results also show that the acetone and MEK concentrations in the kraft hardwood pulping process did not decrease until very late in the cooking process for unknown reasons as shown in Fig. 5b. Further study is needed to understand the reaction mechanism. Figures. 4b and 5b also show that more acetone than MEK is formed in both kraft and soda pulping of a hardwood and a softwood.

It was also found that further extending the cooking process beyond 3 hours can result in a decrease in methanol and ketone concentrations, as shown in Figs. 4 and 5. The decrease in concentrations is probably related to condensation.

VOC Formation During Pulping of Kenaf

Figure. 6 shows the formation of methanol, acetone, and MEK in the soda-AQ pulping of kenaf bast and core. It was found that the cooking of kenaf core produced much more methanol than the cooking of bast. This is because kenaf core has a much higher lignin content (about 17%) than that of bast (about 7%) [16]. Kenaf does not contain hemicellulose [16], which means that all the methanol is formed through the demethylation of lignin. Therefore, the kinetic data on lignin demethylation are critical to estimate methanol formation using Eqn. (7). Unfortunately, little data about the molecular structure of kenaf lignin and lignin demethylation kinetics are available in the literature; therefore, the calculation of methanol formation during kenaf pulping was not performed. However, the experimental data does show that more methanol was formed in the pulping of kenaf core than in kenaf bast as the core has a higher lignin content than bast has.

The behaviors of ketone formation in the soda-AQ pulping of kenaf core are similar to those of kraft pulping of hardwood. The peak concentrations of ketones in bast pulping were shifted to a later pulping time compared to those in the pulping of core.

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Effect of Catalyst on VOC Formation

We conducted two sets of experiments to evaluate the effect of a catalyst, anthraquinone (AQ), on VOC formation during pulping. We found that the methanol concentrations were essentially identical for the first hour of all cooking processes studied, as shown in Figs. 7 and 8. The significant differences in methanol formation with or without AQ is only at the later stage of the pulping processes when the cooking temperature is high (170°C). The catalyst increased the formation of methanol by 15% in softwood kraft pulping, as shown in Fig. 7, while an opposite phenomenon is observed in hardwood kraft pulping, i.e., the catalyst reduced the formation of methanol by about 10%, as shown in Fig. 8.

As discussed previously, methanol is formed through two mechanisms, i.e., degradation of xylans in the hemicellulose and the demethylation of lignin, as represented by reactions (1a) and (1b), respectively. According to Wilson et al. [9], xylan degradation is the dominant methanol formation mechanism. As proposed by Clayton [7], xylan degradation in alkaline pulping of wood is brought about by the conversion of 4-O-methyl-D-glucuronic acid groups present in xylans into the corresponding unsaturated acids. This postulation was later verified by Johansson and Samuelson [17]. They found that a model compound of xylan, 2-O-(4-O-methyl-D-glucopyranosyluronic acid)-D-xylitol can react with sodium hydroxide (1 M) at 150°C to yield 50% hexeneuronic acid after a 90-minute reaction time. The reaction also forms methanol at the same time. This indicates that xylans can be partially degraded and form methanol at a high pulping temperature. In pulping, the formation of methanol from xylans is mainly in the early stage of the cooking. Holton confirmed that the AQ possesses a marked capability of accelerating the delignification and leads to an increase in pulp yield [18]. On the other hand, Lowendahl and Samuelson [19] indicated that AQ has the ability to stabilize polysaccharides, such as xylan, toward alkaline degradation. Hardwood has a high xylan content (15-30%) and a low lignin content (18-25%) [11]. The effect of stabilization of xylans is probably significant enough to slow down the reaction (1a) in AQ pulping of hardwood, therefore, less methanol is formed, as shown in Fig. 8. Softwood has a low xylan content (5-10%) and a high lignin content (25-35%) [11], therefore, delignification acceleration is perhaps more significant than the stabilization of xylan degradation by AQ, producing more methanol in softwood pulping.

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SUMMARIES

This report presents the concentration profiles of three major water-soluble, steam-volatile organic compounds, i.e., methanol, acetone, and MEK, during conventional pulping processes. These compounds are mainly formed in the initial stage of the cook at a temperature of 170°C. More methanol can be produced in hardwood pulping processes than in softwood. Kraft pulping processes produce more methanol than soda processes. A methanol mass balance calculation based on 100% hydrolysis of methoxyl groups in xylan indicate that hemicellulose degradation accounts for about 75% of the methanol formed in pulping. The demethylation of lignin accounts for about 20% of the methanol formed based on a ~2% lignin methoxyl group conversion given in the literature. Kinetic analysis indicates that the overall methanol formation reaction follows Arrhenius kinetics well. The formation behaviors of acetone and MEK in the processes are different from that of methanol. These ketones have probably undergone a hemiacetal or hemiketal reaction with methanol in most pulping processes. We found that wood species also contributed to the differences in the formation of these volatile compounds in pulping.

ACKNOWLEDGEMENT

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Fig. 1

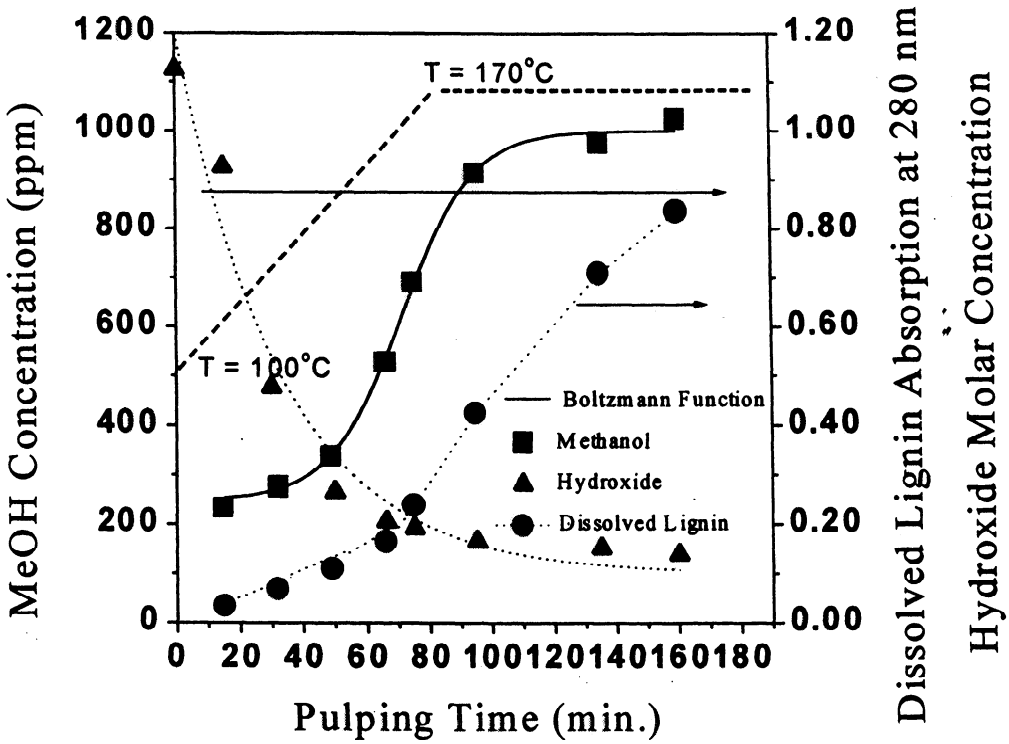
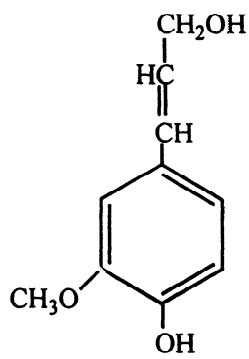
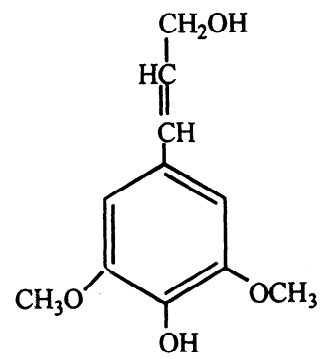


Fig. 2



Coniferyl alcohol



Sinapyl alcohol

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Fig. 3

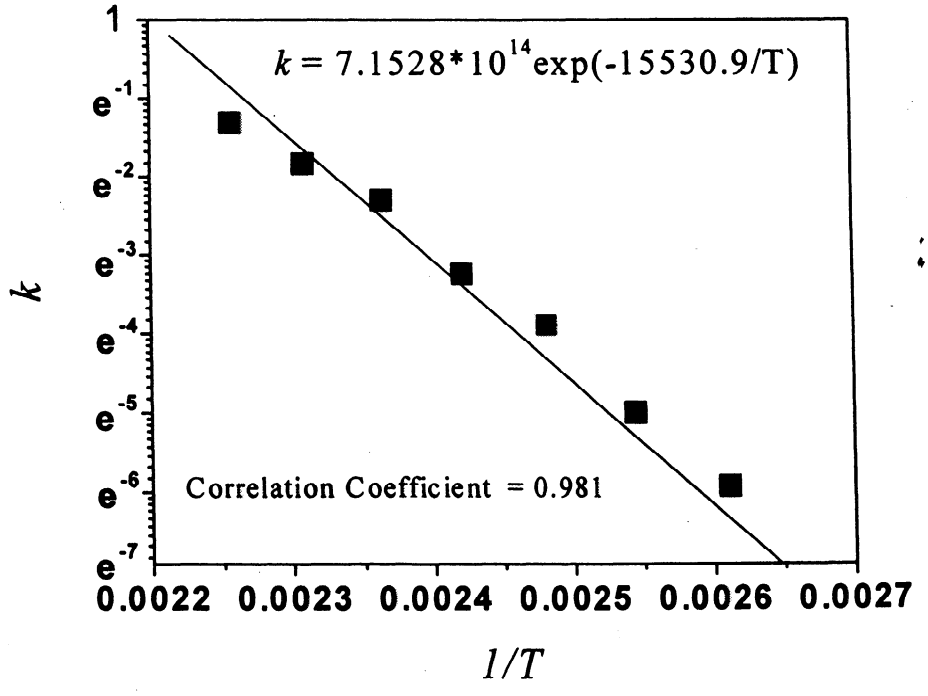

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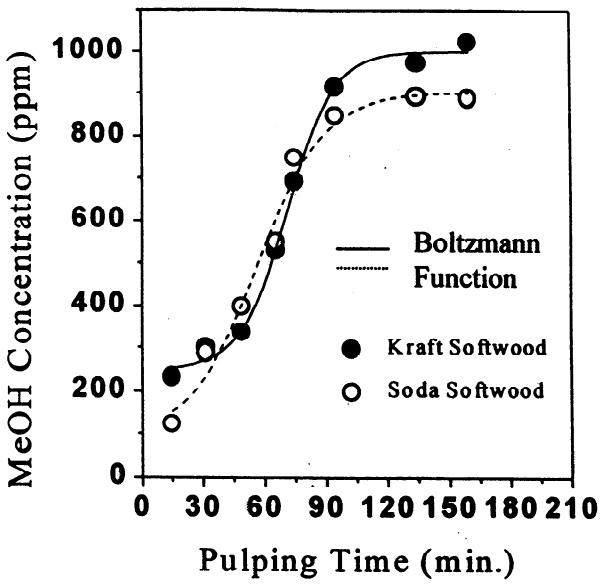
Fig. 4



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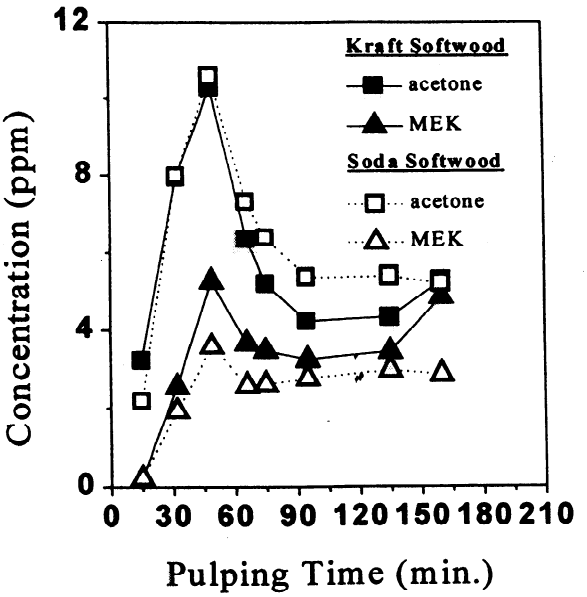
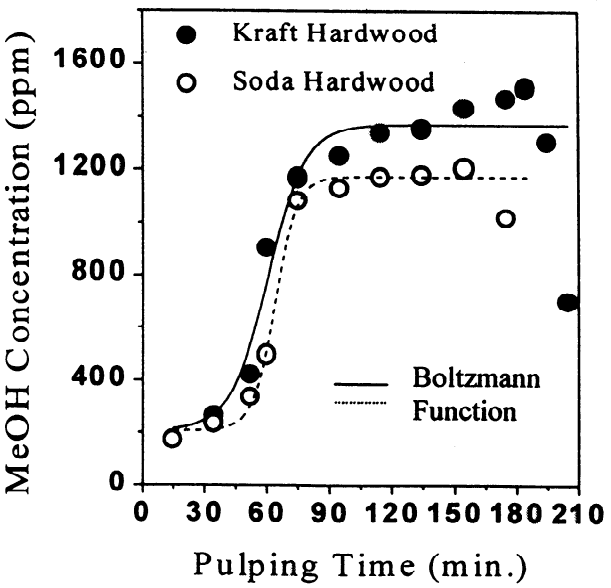


(b)

Fig. 5



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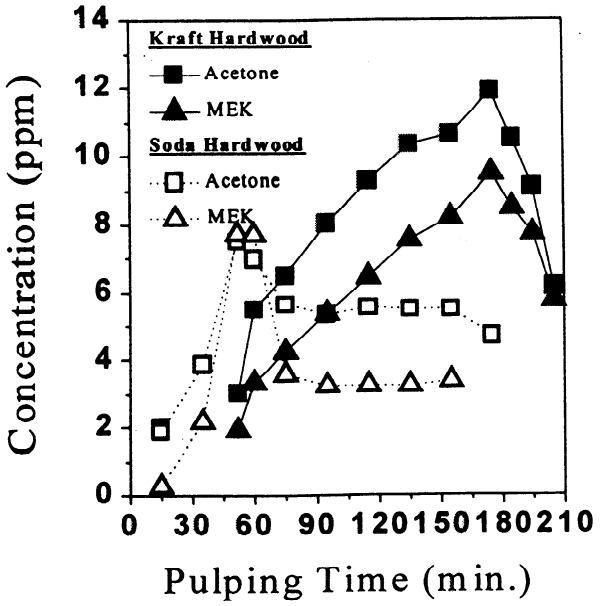

(b)

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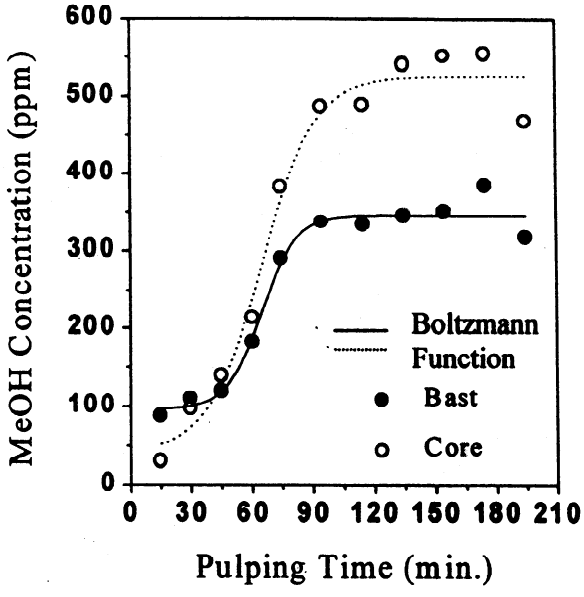
Fig. 6



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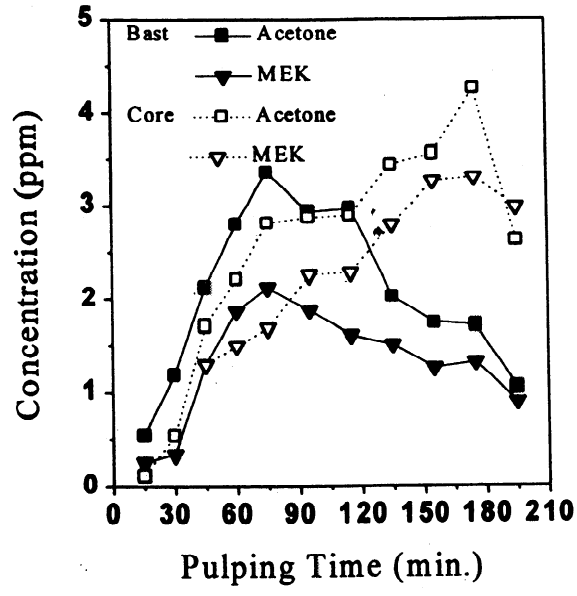

(b)

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Fig. 7

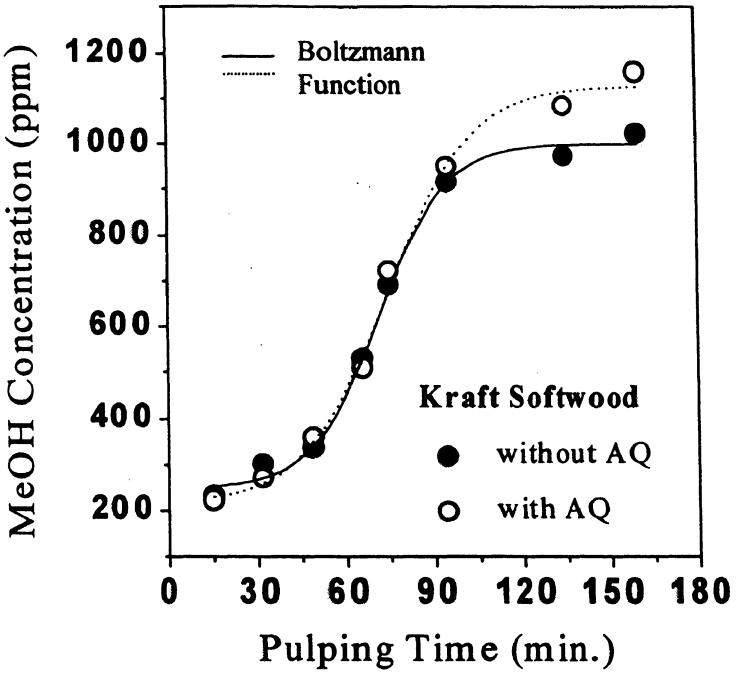

Fig. 8

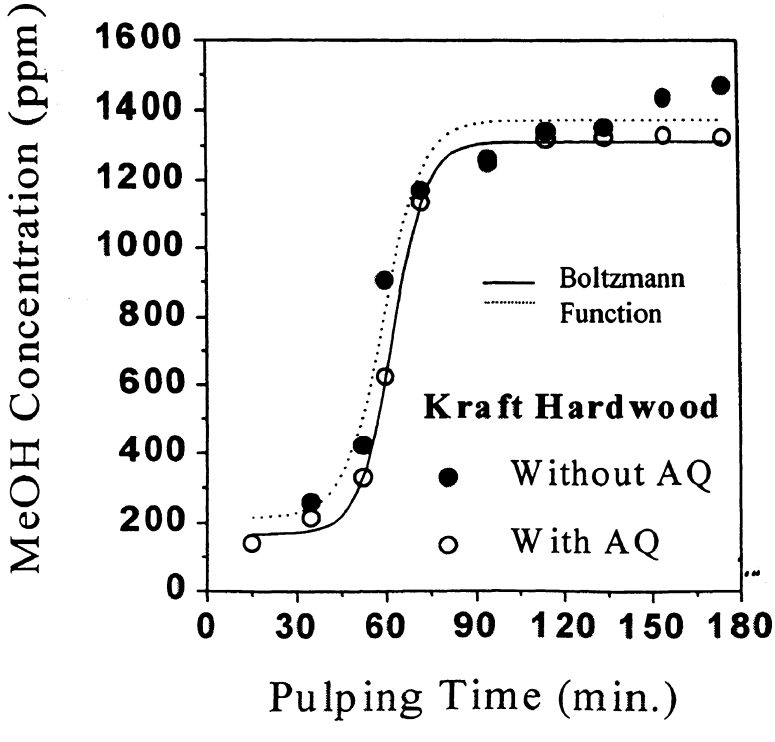

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Table I: A list of pulping conditions.

PARAMETERS	VALUES
Alkali (%)	18
Sulfidity (%)	0 for soda 25 for kraft
Liquid-to-Wood Ratio	4 for softwood and hardwood 8 for kenaf bast and core
Final Temperature (°C)	170
H Factor	2000
Catalyst	None and AQ for Woods AQ only for Kenaf

Table II: A list of final kappa numbers following the pulping processes.

Pulping Material	Kappa Number	
	Kraft Pulping	Soda Pulping
Softwood	28 (with AQ) 31 (without AQ)	31 (with AQ) 34 (without AQ)
Hardwood	14 (with AQ) 15 (without AQ)	16 (with AQ) 18 (without AQ)
Kenaf: Bast	N/A	8 (with AQ)
Kenaf: Core	N/A	16 (with AQ)

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Table III: Calculated methanol concentrations in the final cooking liquors of birch and pine.

Parameters	Birch	Pine
Xylan content (x_{xylan})*	0.15-0.30	0.05-0.10
Ratio of 4-O-Methyl-Glucuronic Acid to xylose ($R_{me\text{-}glu\text{-}acid}$)**	0.1	0.17-0.33
Fraction of 4-O-Methyl-Glucuronic Acid hydrolyzed (f)	1.0	1.0
Calculated methanol concentration due to xylan demethylation (mg/L)***	937	781
Experimentally measured concentration in this study (mg/L)	1330	1020
Xylan demethylation contribution	70%	77%

* The average values of 0.225 and 0.075 were used in the calculation for birch and pine, respectively.

** The average value of 0.25 was chosen in the calculation.

*** The molecular weight of methanol and the 4-O-methyl-glucuronic acid of xylan are M_{MeOH} = 31 and $M_{me\text{-}glu\text{-}acid}$ =186, respectively. The liquid-to-wood ratio is R_{LW} = 4.

Table IV: Calculated methanol concentrations in the final cooking liquors of birch and pine.

Parameters	Birch	Pine
Lignin Content (x_{lignin})*	0.18-0.25	0.25-0.35
Ratio of coniferyl alcohol to lignin ($R_{Conf\text{-}alcoh}$)*	0.50-0.75	1.0
Ratio of sinapyl alcohol to lignin ($R_{Sinp\text{-}alcoh}$)*	0.25-0.50	0
Fraction of lignin demethylated (q)	q_c=0.015 q_{s1}=0.027 q_{s2}=0.027	q_c=0.015
Calculated methanol concentration due to lignin demethylation (mg/L)**	255	197
Experimentally measured concentration in this study (mg/L)	1330	1020
Lignin demethylation contribution	19%	19%

* The average values of 0.215, 0.62, and 0.38 were used for x_{lignin}, $R_{Conf\text{-}alcoh}$, and $R_{Sinp\text{-}alcoh}$, respectively, in the calculation.

** The molecular weight of methanol, coniferyl alcohol, and sinapyl alcohol are M_{MeOH} = 31, $M_{Conf\text{-}alcoh}$ =177, and $M_{Sinp\text{-}alcoh}$ =198, respectively. The liquid-to-wood ratio is R_{LW} = 4.

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Table V. Methanol mass balance.

Parameters	Birch	Pine
Xylan Contribution (mg/L)	937 (70%)	781 (77%)
Lignin Contribution (mg/L)	255 (19%)	197 (19%)
Total Calculated (mg/L)	1192 (90%)	978 (96%)
Total Experimentally Measured (mg/L)	1330	1020
Unaccounted (mg/L)	138 (10%)	42 (4%)

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DUES-FUNDED PROJECT SUMMARY

Project Title:	Gasification of Black Liquor
Project Code:	
Project Number:	F028
PAC:	Chemical Recovery
Division:	Chemical Recovery and Corrosion
Project Staff	
Faculty/Senior Staff:	Kristiina Iisa, Scott Sinquefield
Staff:	Qun Jing
FY 99 Budget:	$131,000
Allocated as Matching Funds:	None
Time Allocation	
Faculty/Senior Staff:	K. Iisa 33 %, Scott Sinquefield 40%
Support:	Q. Jing 50 %
Supporting Research	
M.S. Students:	Steve Horenziak: Fate of Sulfur During Black Liquor Gasification
Ph.D. Students:	None
External:	4260 Fundamental Study of Black Liquor Gasification Kinetics Using a Pressurized Entrained-Flow Reactor
Exploratory:	None
RESEARCH LINE/ROADMAP:	- Improved Capital Effectiveness. 8. Develop technologies to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity by 30 % without adding Tomlinson recovery boilers. - Energy performance. 10. Reduce net energy consumption per ton by 30 % compared to '97 levels.

PROJECT OBJECTIVE:
The objective of the project during FY98-99 has been to study the kinetics of inorganic species transformations during black liquor gasification. The inorganic species investigated are sodium, potassium and chlorine.

PROJECT BACKGROUND:
Black liquor gasification is being developed as a replacement for traditional recovery boilers. Commercial development has concentrated on conversion of the organic matter to a fuel gas. Relatively little attention has been given to the fate of contaminants such as K, Cl and N. The fate of these elements along with the fate of sulfur, and sodium as well as tars formation will be important to the cost and operability of a black liquor gasifier.

GOALS FOR FY99:
1) Complete atmospheric studies of the fate of Na, K and Cl during gasification by CO_2, H_2O and combined CO_2/H_2O gasification. The effect of temperature, time and gas concentrations will be evaluated.
2) Conduct first pressurized gasification experiments, including reproducibility tests and material balance closure evaluation.

DELIVERABLES (FY99):
Data and report detailing impact of gasification conditions on a) fume formation, b) Cl and K enrichment factors, and c) chlorine purge and HCl emissions at atmospheric conditions. Proven feasibility of using the pressurized entrained-flow reactor for studies of black liquor gasification.

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PROJECT PROGRESS AGAINST FY99 GOALS:

The atmospheric study of Na, K, and Cl during CO_2 gasification has been completed and a member report on these experiments is under progress. 40% of the atmospheric H_2O gasification experiments have been completed but none of the chemical analyses. The experiments and chemical analyses will be finished by the end of FY99. The data interpretation on H_2O gasification experiments will be finished and a member report will be issued during early fuscal year 2000. The pressurized entrained-reactor will be ready for first tests in April-May.

SUMMARY OF RESULTS MARCH 98-FEBRUARY 99

Black liquor gasification experiments were made in an atmospheric laminar-entrained flow reactor (LEFR). In the LEFR, solid particles are entrained in a gas flow and introduced into the reactor, in which they are rapidly heated to the furnace temperature. The particles and gases exit through a collector, in which they are rapidly quenched. The particle residence time, furnace temperature and gas composition can be controlled independently. Large particles form the off-gases are separated in a 3-um cut-size cyclone, and smaller particles on a filter.

The liquor used in the experiments contained 19.0% Na, 1.7% K, 0.43% Cl and 4.4% S. Preliminary studies showed that the fume formation in the LEFR depended on the solid feed rate. The impact was largest at low liquor feed rates but negligible at feed rates above 0.2 g/min. The liquor feed rates were kept above 0.2 g/min in the rest of the experiments. The temperature was varied in the range 700-1100°C and the CO_2 and H_2O concentrations in the range 5-20%. The residence time of the particles was varied from 0.6 s to 1.4 s. Both the cyclone catch particles, i.e. particle residues, and the filter paper catch particles, i.e. fume, were collected and analyzed for potassium and sodium by ICP (inductively coupled plasma) and for chloride by CES (capillary electrophoresis system).

All of the LEFR experiments with CO_2 as the gasifying agent have been completed. At 700-900°C, less than 5% of both Na and K became volatilized in the residence time range studied (see Figure 1 and Figure 2). At higher temperatures, the vaporization became significant, and 30% of Na, and 40-50% of K became vaporized at 1100°C, the highest temperature studied. The K enrichment factors varied in a range of 1.5-2.2. The enrichment factor was highest at 900°C and decreased as temperature was either lowered or lowered from 900°C (Figure 3).

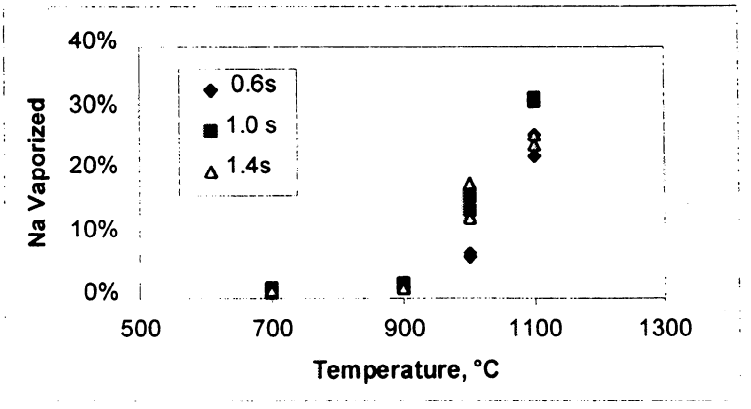

Figure 1. Vaporization of Na as a function of temperature. 15% CO_2, 4% CO, rest N_2.

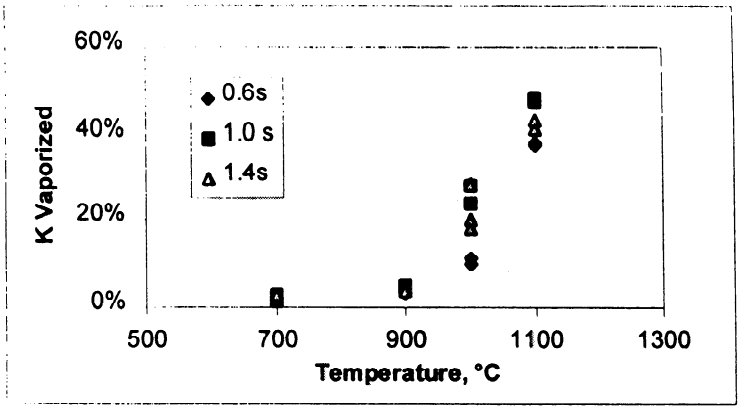

Figure 2. Vaporization of K as a function of temperature. 15% CO_2, 4% CO, rest N_2.

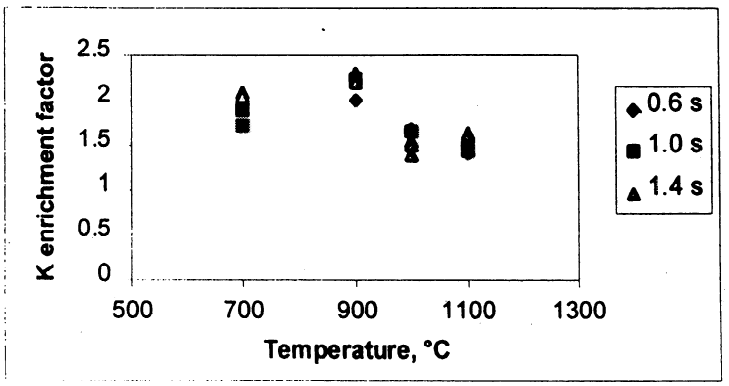

Figure 3. K enrichment factor as a function of temperature. 15% CO_2, 4% CO, rest N_2.

The amounts of both sodium and potassium vaporized decreased as the CO_2 concentration was increased (Figure 4). Two mechanisms are responsible for Na and K volatilization: vaporization of alkali metal chlorides and reduction of alkali metal phenolate groups. CO_2 is a product of the the reduction of the phenolate group. Therefore, CO_2 is expected to suppress the volatilization of alkali metals by this mechanism. This suppression had not been earlier verified experimentally. Additional experiments showed that also CO suppressed the volatilization of Na and K. This had also been hypothesized from the mechanism of alkali metal catalyzed gasification but had not been verified either. The K enrichment factor was relatively independent of the CO_2 concentration.

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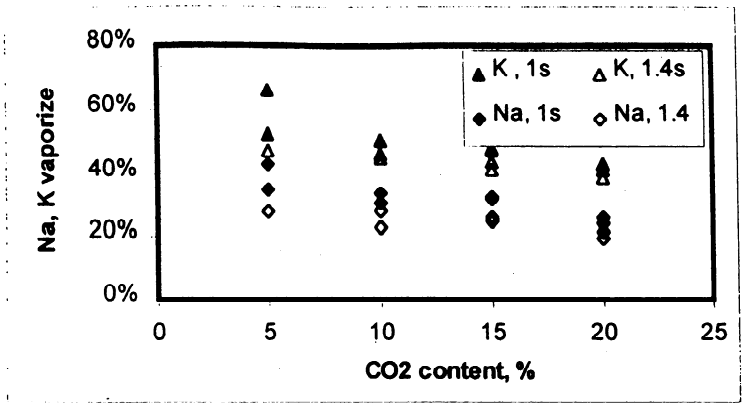

Figure 4. Vaporization of Na and K as functions of CO_2 concentration. Furnace temperature 1100°C; 5-20% CO_2, 4% CO, rest N_2.

The fraction of liquor Cl that was found in the fume ranged from less than 5% to above 90% (see Figure 5). The highest fractions of liquor Cl in the fume were at 1000-1100°C and the lowest at 700°C. At 1100°C, the highest temperature studied, the fraction of liquor Cl in the fume decreased with time (see Figure 6). Chlorine is released into the vapor phase through the evaporation of sodium chloride and potassium chloride. The chlorides in fume can be further converted into hydrochloric acid in the presence of H_2S ($2NaCl + H_2S \rightarrow Na_2S + 2HCl$) or SO_2 ($2NaCl + SO_2 + ½ O_2 \rightarrow Na_2SO_4 + 2HCl$). Corresponding studies of the sulfur species have shown that H_2S is the major gaseous sulfur species during CO_2 gasification. The decrease in the fume Cl at 1100°C can therefore be attributed to the conversion of alkali metal chlorides to HCl. At 1000°C, the Cl in the fume increased from 0.6 s to 1.0 s but decreased from 1.0 to 1.4 s. Thus the rate of NaCl/KCl volatilization exceeded the rate of HCl formation at the short times but at the longer times the HCl formation was more dominant. At 900°C, there is similarly a maximum in the amount of Cl in the fume though the fractions of liquor Cl in the fume were considerably lower at 900°C than at 1000-1100°C. At 700°C, however, the Cl in the fume increased in the range of residence times studied.

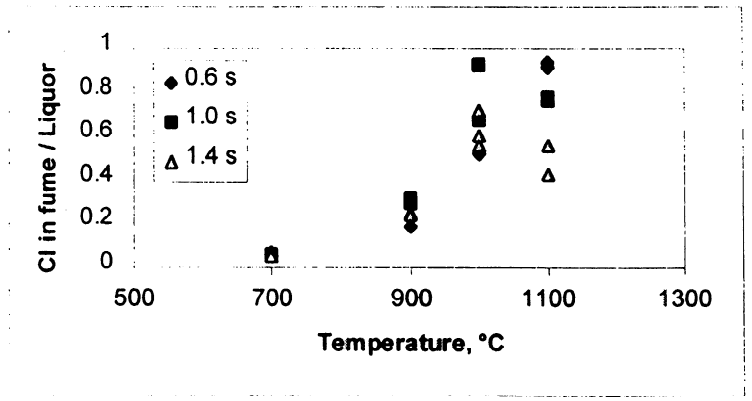

Figure 5. Conversion of liquor Cl to fume Cl as a function of temperature. 15% CO_2, 4% CO, rest N_2.

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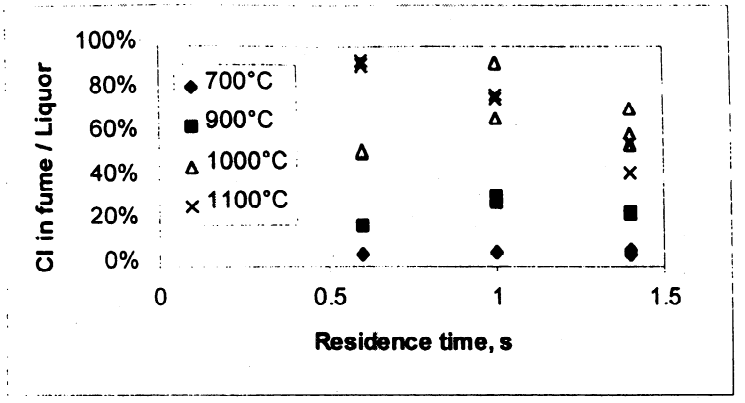

Figure 6. Conversion of liquor Cl to fume Cl as a function of residence time. 15% CO_2, 4% CO, rest N_2.

The chlorine enrichment factor varied between 2 and 15. The enrichment factors were low at the lowest and highest temperatures, and there was a maximum with respect to temperature at 900°C (see Figure 7). The fraction of liquor Cl in the fume decreased only from 1000 to 1100°C Thus the decrease in the effectiveness factor is for a major part due to the increases in Na and K volatilization at the higher temperature. The Cl enrichment factor increased with residence time at 900°C but decreased at higher temperatures.

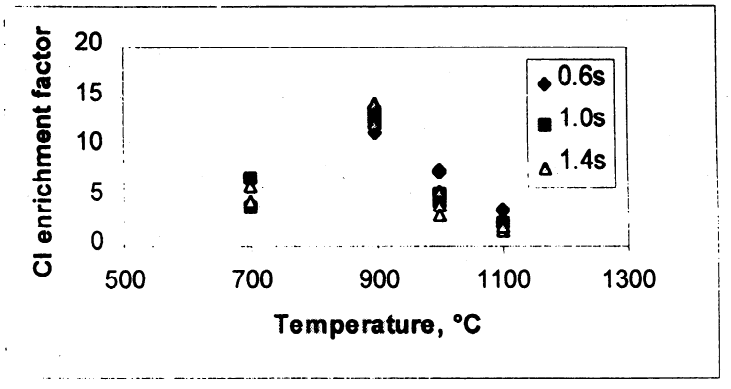

Figure 7. Cl enrichment factor as a function of temperature. 15% CO_2, 4% CO, rest N_2.

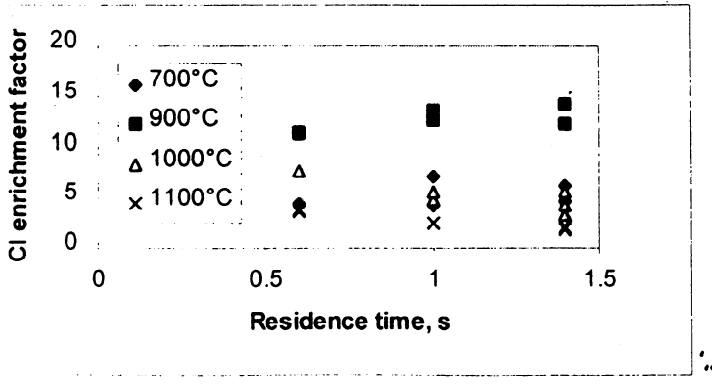

Figure 8. Cl enrichment factor as a function of residence time. 15% CO_2, 4% CO, rest N_2.

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The CO_2 content affected the fume Cl content as well. At 1100°C, the fraction of liquor Cl in the fume varied from 40 to over 90% (Figure 9). At all other CO_2 contents except the highest (20%), the fume Cl decreased with residence time. The conversion of alkali metal chlorides to HCl was thus significant. With 20% CO_2 the gasification was complete both at 1 s and 1.4 s. It is possible that the lack of impact of residence time at this condition is because no more sulfur was released from the liquor, and all sulfur available for NaCl/KCl conversion had reacted by 1 s. The fraction of Cl in the fume at a given residence time, decreased as CO_2 content was increased in the range 5-15%. This may be due to more S being available to react with NaCl/KCl as the CO_2 content increased.

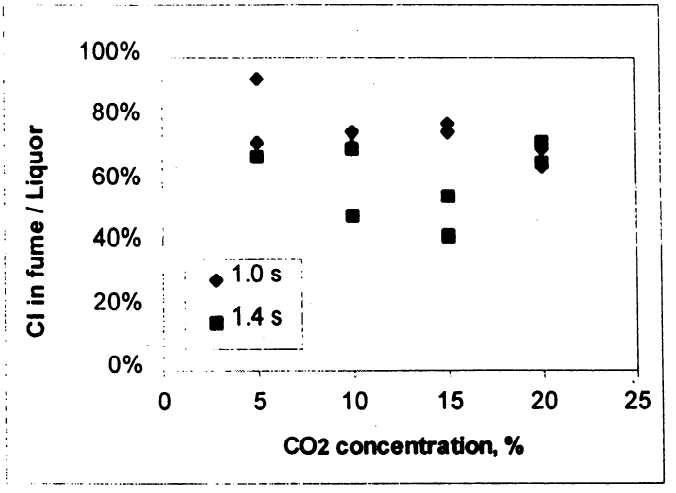

Figure 9. Conversion of liquor Cl to fume as a function of CO_2 content. Temperature 1100°C; 5-20% CO_2, 4% CO, rest N_2.

The Cl enrichment factor varied between 1.7 and 3.6 at the different CO_2 contents (see Figure 10). Thus the effect of CO_2 on the enrichment factor was far less than the effect of temperature. With a residence time of 1.0 s the Cl enrichment factor slightly increased as the CO_2 concentration increased. However, the behavior at 1.4 s was more complex. Both Cl in the fume and alkali metal volatilization affect the enrichment factor. CO_2 suppresses alkali metal volatilization and therefore increases Cl enrichment. This contributes to the trend of Cl enrichment increasing with CO_2 content even though the fraction of Cl in the fume may have decreased.

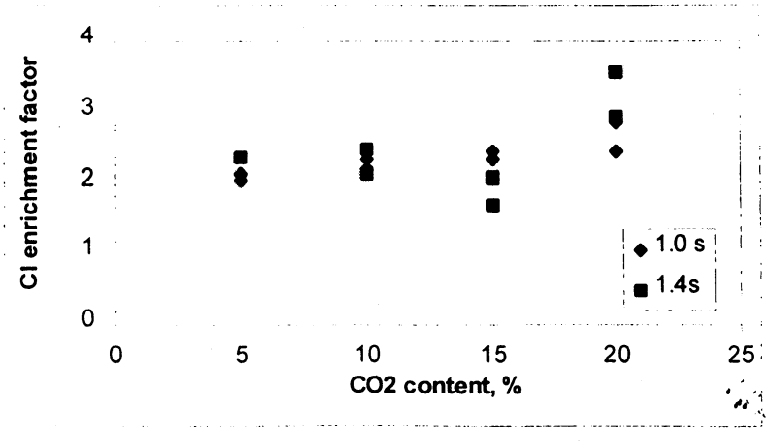

Figure 10. Cl enrichment factor as a function of CO_2 concentration. Temperature 1100°C; 5-20% CO_2, 4% CO, rest N_2.

Of the investigation with H_2O as a gasifying agent, experiments with different levels of H_2O have been completed. The temperature was 1100°C and the residence time 1.4 s. The char and fume yields for these experiments are shown in Figure 11. The gasification was complete at all of the data points and thus the data present the final char and fume yields from gasification by H_2O. The fume yield varied from 4 to 7%. It was highest at an H_2O content of 10%. The fume yields are clearly lower than for gasification by CO_2 for which they were 10-14% at the same temperature and residence times and corresponding CO_2 concentrations. Within the scatter of the data the char yields with H_2O were constant at approximately 40%. The char yields are higher than the corresponding char yields for gasification by CO_2, which were 15-32%. The char and fume have not been analyzed and further conclusions from the data can not be drawn yet.

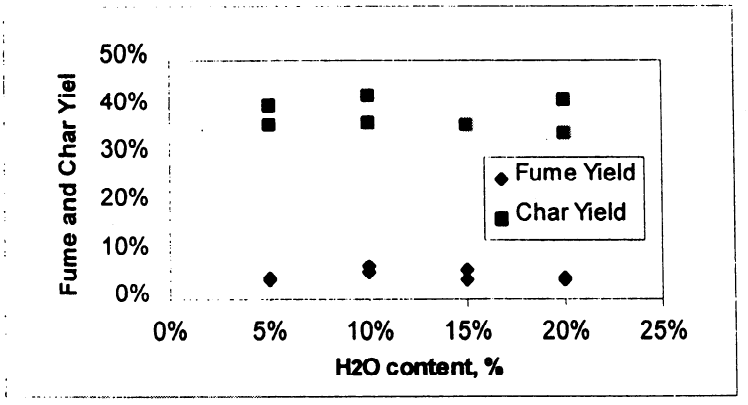

Figure 11. Fume and char yield for gasification by H_2O. Furnace temperature 1100°C, residence time 1.4 s, 5-20% H_2O, rest N_2.

PLANS FOR MARCH 99-SEPTEMBER 99

Atmospheric work:

The H_2O gasification experiments will be finished. This includes experiments at different temperatures and residence times at a constant H_2O level. Limited experiments with both CO_2 and H_2O in the gas phase will be made. The chemical analyses of the new and existing samples will be finished. Besides Na, K and Cl, measurements will be made to identify the S compounds in the gas and solid phases during H_2O gasification. Steve Horenziak has studied in his MS project the fate of sulfur compounds during gasification by CO_2 but the fate of sulfur during H_2O gasification has not been investigated.

Pressurized work:

The pressurized gasification experiments will be begun during the spring. The first task is to test the reproducibility of the experiments and material balance closures. The initial tests will be made with activated carbon, and after they are successful black liquor will be employed in the experiments. To close the material balances, the particle residues and gas phase compounds will be measured. A combination of gas chromatography, Fourier-transform infra-red and regular infra-red spectroscopy will be used to analyze the gas phase. In the current configuration, the particle residues and fume are collected separately on a filter. In order to separate the particle residues from the fume particles, high-pressure cyclone(s) will be added to the equipment. The elements for which the material balance closure will be tested are carbon (for activated carbon and black liquor) and Na and K (for black liquor).

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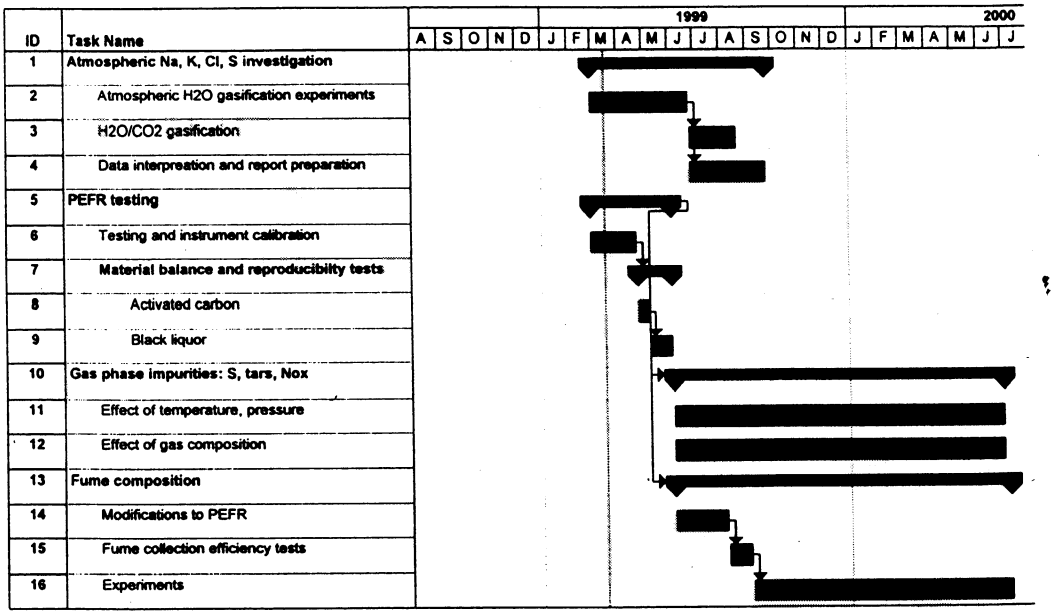
The first investigation with the pressurized entrained-flow reactor will include characterizing the trace impurities in the gas phase including sulfur compounds, NOx and NOx precursors and tars. The effects of temperature, residence time, gas atmosphere and pressure will be tested.

Figure 12. Gantt chart for March 99 through June 00.



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